THE EXTRA SPOTS ON THE LAUE PHOTOGRAPH.

THESIS

SUBMITTED BY

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FOR THE DEGREE OF Ph.D.

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Introduction.

Recent research on X-ray scattering by crystals has shown that the back-ground of luminosity on Laue photographs is not structureless, but consists of certain well defined spots and streamers. (Raman and Nilakanton, 1940, Bragg 1940, Lonsdale 1941, Preston 1941). The extra spots differ from the Laue spots in that they do not correspond to definite positions of the crystal relative to the incident beam. However, the researches of Mrs. Lonsdale have shown that the extra spots lie in the neighbourhood of Laue spots and have the greatest intensity when the crystal is only slightly turned from a position which would give a Bragg reflection. She suggests that the positions of the extra spots merely form a pattern similar to that formed by the Laue spots, but slightly displaced on the photographic plate. A very good photograph showing this effect is given in 'Nature' (147, p. 467). Another difference between the two types of spot is the temperature effect. By decreasing the temperature the Laue spots become much more intense, and photographs taken at liquid air temperature show them much more clearly than those taken at ordinary temperatures. On the other hand, the intensity of the extra spots decreases with decrease in temperature, and, in fact, experiments carried out at liquid air temperatures give no extra spots on the photographic plate.

There have been several theories put forward to explain this phenomenon, particularly by Bragg and Preston, Raman and Nilakantan, and Faxen.

Professor Born has considered the effect that would be produced by the electronic excitation wave. Although it was found that this would produce maxima in the intensity of the scattered light, apart from the Laue spots, the maxima were not sufficiently sharp, nor bright to be observed.

The effect which is produced by the vibrations of the atoms of the substance under consideration, was developed in a paper by Professor Born and myself, (In Press for P.R.S.) and the results obtained appear to agree with observation.

Sections (1) and (2) contain a part of this paper and I have to thank Professor Born for allowing me to use it. Section (3) deals with the temperature effect on the scattering. The equations obtained in §1 and §2 are too general to allow an exact discussion of the position of the extra spots. Consequently certain assumptions have to be made. In §4 the positions of the extra spots, and the shape of the spots are considered for a diagonal lattice (Born, 1923 §13) under the simplifying assumption that the effects of anisotropy can be neglected.

In section (5) we make the simplification of considering only directions of scattering which lie in the plane $\eta=0$.

I take this opportunity to express sincerest thanks to Professor Born under whose guidance I have done my research.

1. Scattering of X-rays by an atomic system.

A system consisting of N particles having the equilibrium position vectors $\underline{r}_k$, $(k = 1, 2 \ldots N)$ is considered. Each particle is displaced by thermal motion, the k^{th} to the position $\underline{r}_k + \underline{u}_k$ say, where $\underline{u}_k$ is small.

The directions of the incident and scattered X-ray beams are defined by the unit vectors $\underline{s}$ and $\underline{s}'$ respectively so that

$$|\underline{s}| = 1, \qquad |\underline{s}'| = 1, \qquad (\underline{s}.\underline{s}') = \cos\theta, \qquad (s - s')^2 = 2(1-\cos\theta).$$

where θ is the angle between the incident and scattered beam.

The quantities $\underline{k}$ and $\underline{k}'$ are introduced by means of

$$\underline{k} = \frac{2\pi}{\lambda}\,\underline{s} \quad , \qquad \underline{k}' = \frac{2\pi}{\lambda}\,.\,\underline{s}' .$$

λ is the wave length of the incident X-rays and it is assumed to be practically unchanged by scattering. However the small changes in the frequency which are produced on account of the excitation of the electrons of the atoms are not completely neglected since they are responsible for the incoherence of the different components of the scattered intensity, which is taken into account in the problem.

The different quantum states of the whole vibrating system are distinguished by a quantum number n which stands symbolically for a set of $(3N-3)$ numbers, $n_1, n_2 \cdots$. It will be noted in passing that this ($(3N-3)$) arises from the fact that the system has to be considered as only having ($(3N-3)$) degrees of freedom; For such vibrations of the particles as would just give the whole system a displacement must be omitted. This is because such a vibration corresponds to zero frequency and consequently does not give rise to a quantum mechanical problem. This reduces the total number of co-ordinates by three. Connected with each state n of the system there exists a probability $W(n)$, a function of $n_1, n_2 \cdots$ of finding the system in this state. Under the action of the incident light the system can make transitions to all possible other states n' . The distribution of the final state, corresponding to a definite initial state n will be determined by means of the selection rules of the system. During the transition $n \to n'$ the system emits radiation which is proportional to $|M(n,n')|^2$ where M is the electric moment and depends on the amplitude, correctly retarded, of the incident wave, and $M(n,n')$ is the matrix element of the operator M i.e. is equal to $(\psi_n, M\,\psi_{n'})$, ψ_n being a wave function of the vibrating system. Placzek has shown, that for a crystal whose dimensions are small compared with its distances from the source and from the observer, (as is always the case in the practical work),

$$(1.2) \qquad M = \sum_k \alpha_k E_0 e^{i(\underline{K}-\underline{K}' \cdot \underline{r}_k + \underline{u}_k)}.$$

omitting all effects of polarization. α_k is the polarisability of the atom k which Placzek proved to be a function of the displacements of the other atoms. By a quantum mechanical consideration of the electrons and nuclei of the atoms he has, in fact, shown that α_k can be expanded in a series of the $\underline{u}_k$ thus:-

$$\alpha_k(u) = \alpha_k^0 + \sum_{k'y} \alpha_{kk'y} u_{k'y} + \cdots$$

Working on such a hypothesis, the effect that the term $\sum_{k'y} \alpha_{kk'y} u_{k'y}$ would have on the intensity of the scattered light was calculated. It was found to be small, and the fluctuations in the intensity were not sharp enough to give spots as definite as those which do appear in the background of the Laue photograph. We shall thus neglect this effect, i.e. what we actually neglect is the change in frequency of the scattered intensity, for we neglect the energy communicated to the system in causing the atomic electrons to jump to higher quantum states. However, as has been stated earlier, the effect is not entirely neglected, since we do take into account the incoherence of the different components of scattered radiation.

α_k can be calculated with the help of the dispersion formula of quantum theory, and it can be expressed in the form

$$\alpha_k = \alpha_0 f_k , \tag{1.3}$$

Where α_0 is the polarisability due to the free electron, and f_k is the atomic scattering factor. If we define

$$f = \sum_k f_k \, e^{i(\underline{K}-\underline{k}' \cdot \underline{r}_k + \underline{u}_k)} , \tag{1.4}$$

then we shall have

$$M = \alpha_0 f ,$$

and

$$|M(n,n')|^2 = \alpha_0^2 E_0^2 \; |f(n,n')|^2 . \tag{1.5}$$

$f(n,n')$ is the matrix element of f .
Thus the intensity of the scattered X-rays corresponding to the transition $n \to n'$ is

$$I_{nn'} = I_0 C \, |f(n,n')|^2 . \tag{1.6}$$

Where $I_0 = E_0^2$ is the intensity of the incident radiation, and C is the Thomson scattering factor

$$(1.7) \qquad C = \frac{1}{r} \cdot \frac{e}{mc^2} \cdot \frac{1+\cos^2\theta}{2} .$$

i.e. it is the scattering power of a free electron through an angle θ .

It is at this point that we take into account the change in the frequency of the scattered intensity. For each transition $n \to n'$ will give rise to scattered intensities of different frequency, and thus the total intensity I is given by

$$(1.8) \qquad I = I_0 C \sum_n \sum_{n'} |f(n,n')|^2 W(n) .$$

Normal co-ordinates ξ_j are now introduced by means of the equations

$$(1.9) \qquad \underline{u}_k = \frac{1}{\sqrt{m_k}} \sum_j \underline{e}_k^j \xi_j ; \qquad \xi_j = \sum_k \sqrt{m_k} (\underline{e}_k^j \cdot \underline{u}_k),$$

Where $\underline{e}_k^j$ is the eigen-vector belonging to the frequency ω_j , and is normalised so that

$$(1.10) \qquad \sum_k \underline{e}_k^j \cdot \underline{e}_k^{j'} = \delta_{jj'} ; \qquad \sum_j e_{kx}^j e_{k'y}^j = \delta_{kk'} \delta_{xy} .$$

and also the $\underline{e}_k^j$ must be chosen so that $\frac{1}{2} \sum_j \omega_j^2 \xi_j^2$

is the same as the second order terms in the potential energy of the displaced system.

But

$$\frac{1}{2}\omega_j^2\xi_j^2 = \frac{1}{2}\sum_j\sum_{kk'}\omega_j^2 (m_k m_{k'})^{1/2}\sum_{xy} e^j_{kx} e^j_{k'y} u_{kx} u_{k'y} .$$

and thus the right-hand side of this equation must be the expression for the potential energy of the displaced system when this is expanded in a power series in $\underline{u}_k$ and terms of higher order than the second rejected.

Now the Hamiltonian, in terms of these coordinates ξ_j and the conjugate momenta $p_j = \dot{\xi}_j$ is

$$H = \frac{1}{2}\sum_j \left(p_j^2 + \omega_j^2 \xi_j^2 \right) , \tag{1.11}$$

i.e. the sum of Hamiltonians of independent harmonic oscillators. Thus the wave function of the whole system is a product of the normalised wave functions of the harmonic oscillator. We shall write it

$$\psi(n,\xi) = \psi(n_1\xi_1)\ \psi(n_2,\xi_2) \cdots \tag{1.12}$$

The number of factors will be $(3N-3)$, for, as stated at the beginning of this section the system has $(3N-3)$ degrees of freedom. The numbers $n_1, n_2 \ldots$ describe the states of the independent oscillators - in the following work this set of numbers will be represented symbolically by the one number n .

Since the ψ are real functions, (Hermite functions), $\psi(n,\xi) = \psi^*(n,\xi)$; and f is an operator involving q -numbers only

$$
\begin{aligned}
f(n,n') &= \int \psi(n,\xi)\, f\, \psi(n',\xi)\, d\xi \\
&= \int \psi(n',\xi)\, f\, \psi(n,\xi)\, d\xi = f(n',n) .
\end{aligned} \tag{1.13}
$$

$$d\xi = d\xi_1 d\xi_2 \cdots \; .$$

Thus

$$\sum_{n'} |f(n,n')|^2 = \sum_{n'} f(n,n')\, f^*(n',n) = |f|^2(n,n) , \tag{1.14}$$

the diagonal element of the matrix $|f|^2$.
Now the expression (1.8) for the total intensity becomes

$$I = I_0 C \sum_n |f|^2(n,n)\, W(n) . \tag{1.15}$$

We must now replace the $\underline{u}_k$ by ξ_j in the expression for f . This becomes

$$f = \sum_k A_k\, e^{i \sum_j L_k^j \xi_j} , \tag{1.16}$$

where for brevity we have written

$$
\left\{
\begin{aligned}
A_k &= f_k\, e^{i(\underline{K}'-\underline{K}).\underline{r}_k} \\
\text{and} \quad L_k^j &= \frac{1}{\sqrt{m_k}} \left(\underline{K}-\underline{K}' . \underline{c}_k^j \right) .
\end{aligned}
\right. \tag{1.17}
$$

Thus

$$|f|^2 = \sum_{kk'} A_k A_{k'}^* \, e^{i(L_k^j - L_{k'}^j)\xi_j},$$

and the expression for the intensity is

$$(1{\cdot}18) \qquad I = I_0 C \sum_n W(n) \sum_{kk'} A_k A_{k'} \int \psi^2(n,\xi)\, e^{i\sum_j (L_k^j - L_{k'}^j)\xi_j}\, d\xi .$$

This integral was evaluated first by a method used by Ott, which involves the use of Bessel and Legendre functions. Professor Born has also solved it by an elegant method, employing the properties of Dirac's density function. It is to be noted that many writers expand the exponential in the integrand in a power series and integrate term by term. They actually evaluate only the second order term - that of the first order vanishes - and then express the result again as that exponential which would give rise to this lowest term if expanded in a power series. Although the final result is the same as that obtained by actually solving the integral, the method of obtaining it is hardly rigorous.

In order to find the value of I, we first express it in its extended form, using the expression (1·12) for the wave function. Thus :-

$$I = I_0 C \sum_{kk'} A_k A_{k'}^* \sum_{n_1 n_2 \ldots} \prod_j W(n_j) \int \psi^2(n_j \xi_j) \, e^{i[L_k^j - L_{k'}^j]\xi_j} d\xi_j$$

$$(1.18') \qquad = I_0 C \sum_{kk'} A_k A_{k'} \prod_j \sum_{n_j} W(n_j) \int \psi^2(n_j, \xi_j) \, e^{i[L_k^j - L_{k'}^j]\xi_j} d\xi_j ,$$

since

$$W(n) = \prod_j W(n_j) .$$

$W(n_j)$ being the probability of the j^{th} oscillator being in the state n_j. Now we make use of the result due to Ott, that when $\psi_n(\xi)$ is the wave function of a linear oscillator, and $W(n)$ the probability of the state n

$$(1.19) \qquad \sum_n W(n) \int \psi_n^2(\xi) \, e^{i\mu\xi} d\xi = e^{-\frac{\hbar\mu^2}{4\omega} \coth \beta/2} ,$$

ω being the frequency of the oscillator, and $\beta = \frac{\hbar\omega}{kT}$, T = the absolute temperature. Thus we obtain

$$(1.20) \qquad I = I_0 C \sum_{kk'} A_k A_{k'}^* \, e^{-U_{kk'}} ,$$

where we have written, for brevity,

$$(1.21) \qquad U_{kk'} = \sum_j \hbar (L_k^j - L_{k'}^j)^2 \frac{\coth \beta_j/2}{4\omega_j} . \qquad \beta_j = \frac{\hbar\omega_j}{kT} .$$

This formula gives correctly the temperature influence for the scattering of molecules. For as T increases from zero $\coth(\beta_j/2)$ increases from unity and becomes very large when T is large. Thus $U_{kk'}$ increases with T and so I, which involves T only in the term $e^{-U_{kk'}}$, decreases as T increases. From physical considerations we see, that, in formula (1·21), a zero vibration must be omitted, since $\frac{\coth(\beta_j/2)}{4\omega_j} \to 0$ as $\omega_j \to 0$. This amounts to the same considerations as were made at the beginning of this section, i.e. the omission of a translation of the whole system.

The Scattering of X-rays by crystal lattices.

Let ($\underline{a}_1, \underline{a}_2, \underline{a}_3$) be the basis vectors of the crystal lattice, and $(\underline{b}_1, \underline{b}_2, \underline{b}_3)$ be those of the reciprocal lattice, so that

$$(2.1) \qquad (\underline{a}_i \cdot \underline{b}_j) = \delta_{ij}$$

We assume the basis contains s particles at the points $\underline{r}_k$, $k = 1, 2 \ldots s$. Then the equilibrium position of any particle of the lattice is

$$(2.2) \qquad \underline{r}_k^l = \underline{r}_k + l_1 \underline{a}_1 + l_2 \underline{a}_2 + l_3 \underline{a}_3 .$$

where l_1, l_2, l_3 are any positive or negative integers.

We consider a crystal similar in shape to a cell, containing $n^3 = N$ cells, and use the cyclic boundary conditions (Born, Atomtheorie des Festen Zustandes 1923). It is well known that when each lattice point $\underline{r}_k^l$ suffers a displacement $\underline{u}_k^l$, the second order terms in the P.E. may be written in the form

$$(2.3) \qquad U_2 = \frac{1}{2} \sum_{xy} \sum_{kk'} S_{ll'} \begin{bmatrix} l-l' \\ kk' \\ xy \end{bmatrix} u_{kx}^{l} u_{k'y}^{l'}$$

where the coefficients $\begin{bmatrix} l-l' \\ kk' \\ xy \end{bmatrix}$ are real and satisfy the relations

$$(2.4) \qquad \begin{bmatrix} l-l' \\ kk' \\ xy \end{bmatrix} = \begin{bmatrix} l'-l \\ k'k \\ yx \end{bmatrix} \quad \text{and} \quad \sum_{k'} S_{l'} \begin{bmatrix} l-l' \\ kk' \\ xy \end{bmatrix} = 0 .$$

The equations for small vibrations with frequency ω_j are thus

$$(2\cdot5) \qquad -\omega_j^2 \, m_k \, u^l_{kx} + \sum_{k'} \sum_{l'} \sum_{y} \begin{bmatrix} l\text{-}l' \\ kk' \\ xy \end{bmatrix} u^{l'}_{k'y} = 0 .$$

These can be solved by introducing the plane waves

$$(2\cdot6) \qquad \underline{u}^l_k = \underline{e}^j_k(q) \, \frac{e^{i(l,q)}}{\sqrt{N}} ,$$

where

$$(l,q) = l_1q_1 + l_2q_2 + l_3q_3 ,$$

and

$$q_\alpha = 2\pi\kappa_\alpha ; \quad \kappa_1, \kappa_2, \kappa_3 \text{ are integers, satisfying } -n/2 \leq \kappa_\alpha \leq n/2 .$$

and the $\underline{e}^j_k(q)$ must satisfy the equations

$$(2\cdot7) \qquad \omega_j^2 \, m_k \, e^j_{kx}(q) - \sum_{k'y} \begin{bmatrix} kk' \\ xy \\ q \end{bmatrix} e^j_{k'y}(q) = 0 ,$$

the coefficients $\begin{bmatrix} kk' \\ xy \\ q \end{bmatrix}$ being connected with $\begin{bmatrix} l\text{-}l' \\ kk' \\ xy \end{bmatrix}$ by means of

$$(2\cdot8) \qquad \begin{bmatrix} kk' \\ xy \\ q \end{bmatrix} = \sum_{l} \begin{bmatrix} l \\ kk' \\ xy \end{bmatrix} e^{-i(l,q)} .$$

In order that the $\underline{e}^j_k$ should have non-trivial solutions the secular determinant of (2·7) must vanish. This gives an equation of the $(3s)^{th}$ degree in ω_j^2, which has $3s$ real positive roots for .

Three of these, the acoustical branch, behave like q^2 for small q. All the rest, the optical branch, assume non-zero constant values as $q \to 0$.

We now introduce complex normal co-ordinates by

$$(2\cdot9)\qquad \begin{cases} \underline{u}^l_k = \dfrac{1}{\sqrt{m_k}} \sum\limits_j \sum\limits_q \underline{e}^j_k(q) \dfrac{e^{i(l,q)}}{\sqrt{N}} \xi_j(q) . \\[2ex] \xi_j(q) = \sum\limits_k \sum\limits_l \sqrt{m_k} \dfrac{\overset{?}{e}^{-i(l,q)}}{\sqrt{N}} \underline{e}^j_k(q) \cdot \underline{u}^l_k . \end{cases}$$

where the $\underline{e}^j_k(q)$ satisfy the ortho-normal relations.

$$(2\cdot10)\qquad \begin{aligned} &\sum_k \underline{e}^j_k(q)\, \overset{*}{\underline{e}}{}^{j'}_k(q) = \delta_{jj'} , \\ &\sum_j e^j_{kx}(q)\, \overset{*}{e}{}^j_{k'y}(q) = \delta_{kk'}\, \delta_{xy} . \end{aligned}$$

and also equations similar to (2·7) namely

$$(2\cdot11)\qquad \omega_j^2\, e^j_{kx}(q) - \sum_{k'} \sum_y \begin{bmatrix} kk' \\ xy \\ q \end{bmatrix} \frac{e^j_{k'y}(q)}{\sqrt{m_k m_{k'}}} = 0 ,$$

the x,y,z axes being a suitably chosen set of rectangular axes fixed in the crystal.

We shall show immediately that the complex co-ordinates $\xi_j(q)$ are not independent, and thus they cannot be treated quantum mechanically as performing independent harmonic oscillations. Using (2·4), (2·8) and also the fact that the coefficients $\begin{bmatrix} l \\ kk' \\ xy \end{bmatrix}$ are real, we have

$$(2\cdot12)\qquad \begin{bmatrix} kk' \\ xy \\ q \end{bmatrix}^* = \sum_l \begin{bmatrix} l \\ kk' \\ xy \end{bmatrix} e^{i(l,q)} = \sum_l \begin{bmatrix} -l \\ k'k \\ yx \end{bmatrix} e^{-i(-l,q)} = \sum_l \begin{bmatrix} l \\ kk' \\ xy \end{bmatrix} e^{-i(l,-q)}$$

$$= \begin{bmatrix} k'k \\ yx \\ q \end{bmatrix} = \begin{bmatrix} kk' \\ xy \\ -q \end{bmatrix}$$

?

Thus, since $\omega_j^2(q)$ are real the equations corresponding to (2·11) for $e_k^{*j}(q)$ are

$$\omega_j^2(q)\; e^{*j}_{kx}(q) - \sum_{k'y} \begin{bmatrix} kk' \\ xy \\ -q \end{bmatrix} \frac{e^{*j}_{k'y}(q)}{\sqrt{m_k m_{k'}}}$$

which are just those satisfied by $\underline{e}^j_k(-q)$

Thus far all k and j

(2.13) $$\underline{e}_k^{*j}(q) = \underline{e}^j_k(-q).$$

consequently we shall have

$$\xi_j^*(q) = \sum_k \mathop{S}_l \sqrt{m_k}\, \frac{e^{i(l,q)}}{\sqrt{N}} \left(\underline{e}_k^{*j}(q) \cdot \underline{u}^l_k \right)$$

$$= \sum_k \mathop{S}_l \sqrt{m_k}\, \frac{e^{-i(l,-q)}}{\sqrt{N}} \left(\underline{e}^j_k(-q) \cdot \underline{u}^l_k \right)$$

ie.

(2.14) $$\xi_j^*(q) = \xi_j(-q).$$

Thus ~~if~~ the two co-ordinates $\xi_j(q)$ and $\xi_j(-q)$ are not entirely independent, Real, independent co-ordinates are obtained by introducing the real and imaginary parts of $\xi_j(q)$ thus

(2.15) $$\xi_j(q) = \frac{1}{\sqrt{2}}\left(\eta_j(q) + i\,\zeta_j(q) \right).$$

The factor $1/\sqrt{2}$ has to be introduced on account of normalising conditions.

Using (2·14),

(2.16) $$\eta_j(q) = \eta_j(-q)\;;\; -\zeta_j(q) = \zeta_j(-q).$$

So that $\eta_j(q)$ and $\xi_j(q)$ can be chosen arbitrarily for just half of q -space, defined for example by

$$(2.17) \qquad -\pi < q_1 \leq \pi, \qquad -\pi < q_2 \leq \pi, \qquad 0 \leq q_3 \leq \pi$$

With, of course, only half the points in the $q_3 = 0$ plane, for example, only that part of the $q_3 = 0$ plane for which $q_2 \geqslant 0$, with a cut along the negative half of the q_1 -axis.

Considering the expression $q_d = \frac{2\pi K_d}{n}$, we see that the total number of independent co-ordinates is $n^3 = N$ for each branch j of the $3s$ vibrations. We shall denote by an accent sums and products which have to be taken over half the q -space only - unaccented sums and product signs mean the whole of q -space is included.

Now the expression for U_2 will become

$$(2.18) \qquad U_2 = \frac{1}{2}\sum_j\sum_q \omega_j^2(q)\,\frac{1}{2}\left\{\eta_j^2(q) + \xi_j^2(q)\right\} = \frac{1}{2}\sum_j\sum_q{}' \omega_j^2(q)\left\{\eta_j^2(q) + \xi_j^2(q)\right\},$$

and so each of the $\eta_j(q)$ and $\xi_j(q)$, for the restricted domain of q -space satisfy the equation of the linear oscillator. The total wave function for the whole system can then be written down

$$(2.19) \qquad \Psi(\eta,\xi) = \prod_{j,q}{}' \phi(n_j(q), \eta_j(q))\, \phi(\bar{n}_j(q), \xi_j(q)),$$

where $n_j(q)$ and $\bar{n}_j(q)$ are independent quantum numbers, and $\phi(n,x)$ is the Hermite function of degree n.

We now express the function f, (1·4) for the crystal in terms of the independent co-ordinates $\eta_j(q)$, $y_j(q)$. It is

$$(2\cdot 20)\quad \begin{aligned} f &= \sum_k \mathop{S}_l f_k\, e^{i((\underline{K}-\underline{K}').(l_1\underline{a}_1+l_2\underline{a}_2+l_3\underline{a}_3))}\, e^{i((\underline{K}-\underline{K}').\underline{r}_k)}\, e^{i(\underline{K}-\underline{K}'.\underline{u}_k^l)} \\ &= \sum_k \mathop{S}_l A_k\, e^{-i(l,Q)}\, e^{i\sum_{j,q} \frac{L_k^j(q)\, e^{i(l,q)}}{\sqrt{N}}\,\xi_j(q)}, \end{aligned}$$

Where, for brevity, we have written

$$(2\cdot 21)\quad \left\{ \begin{aligned} Q_\alpha &= (\underline{K}'-\underline{K}\,.\,\underline{a}_\alpha)\,; \quad \alpha = 1,2,3. \\ (l,Q) &= l_1Q_1 + l_2Q_2 + l_3Q_3. \\ A_k &= f_k\, e^{i(\underline{K}-\underline{K}'.\underline{r}_k)}. \\ \text{and}\quad L_k^j &= \frac{1}{\sqrt{m_k}}\,(\underline{K}-\underline{K}'.\,\underline{c}_k^j(q)). \end{aligned} \right.$$

Thus

$$(2\cdot 22)\quad |f|^2 = \sum_{kk'} \mathop{S'}_{ll'} A_k A_{k'}^*\, e^{i(l-l',Q)}\, e^{i\sum_{j,q} Z_{kk'}^{l-l'}(j,q)},$$

where

$$(2\cdot 23)\quad Z_{kk'}^{ll'}(j.q) = \frac{1}{\sqrt{N}}\left\{ L_k^j(q)\, e^{i(l,q)}\,\xi_j(q) - L_{k'}^{*j}(q)\, e^{-i(l',q)}\,\xi_j^*(q) \right\}.$$

Before we determine the matrix elements of $|f|^2$,

$\sum_q \left(Z_{KK'}^{l-l'}(j,q) \right)$ must be expressed only in terms of those co-ordinates $\eta_j(q)$, $\mathfrak{z}_j(q)$. which are independent.

$$(2\cdot24) \qquad Z_{KK'}^{l-l'}(j,q) = \frac{1}{\sqrt{2}\sqrt{N}} \Big[\left\{ L_K^j(q)\, e^{i(l,q)} - L_{K'}^{*j}(q)\, e^{-i(l',q)} \right\} \eta_j(q) + i \left\{ L_K^j(q)\, e^{i(l,q)} + L_{K'}^{*j}(q)\, e^{-i(l',q)} \right\} \mathfrak{z}_j(q) \Big].$$

and using (2·13), (2·16) and the value of $L_K^j(q)$ by (2·21)

$$(2\cdot25) \qquad Z_{KK'}^{*\,l-l'}(j,q) = Z_{KK'}^{l-l'}(j,-q)$$

Thus we can convert the sum over the whole of q -space in (2·22) tb one over only half the space, and thus express $|f|^2$ in terms of independent $\eta_j(q)$, $\mathfrak{z}_j(q)$..

$$(2\cdot26) \qquad |f|^2 = \sum_{KK'} S_{ll'} \left[A_K A_{K'}^* \, e^{-i(l-l',Q)} \, e^{i \sum_j \sum_q' \left\{ Z_{KK'}^{l-l'}(j,q) + Z_{KK'}^{*\,l-l'}(j,q) \right\}} \right].$$

The quantity $Z_{KK'}^{l-l'}(j,q) + Z_{KK'}^{*\,l-l'}(j,q)$ can be written down immediately. It is

$$(2\cdot27) \qquad Z_{KK'}^{l-l'}(j,q) + Z_{KK'}^{*\,l-l'}(j,q) = M_{KK'}^{l-l'}(j,q)\, \eta_j(q) + N_{KK'}^{l-l'}(j,q)\, \mathfrak{z}_j(q).$$

where

$$M_{kk'}^{ll'}(j,q) = \frac{1}{\sqrt{2N}}\left[\left\{L_k^j(q)\,e^{i(l,q)} + L_k^{*j}(q)\,e^{-i(l,q)}\right\} - \left\{L_{k'}^j(q)\,e^{i(l',q)} + L_{k'}^{*j}(q)\,e^{-i(l',q)}\right\}\right].$$

(2.28)

$$N_{kk'}^{ll'}(j,q) = \frac{i}{\sqrt{2N}}\left[\left\{L_k^j(q)\,e^{i(l,q)} - L_k^{*j}(q)\,e^{-i(l,q)}\right\} - \left\{L_{k'}^j(q)\,e^{i(l',q)} - L_{k'}^{*j}(q)\,e^{-i(l',q)}\right\}\right].$$

Introducing these in the expression for $|f|^2$ we get

(2.26′)
$$|f|^2 = \sum_{kk'} \underset{ll'}{S}\, A_k A_{k'}^* \, e^{i(l-l',q)} \prod_j \prod_q{}' \, e^{i M_{kk'}^{ll'} \eta_j(q)} \, e^{i N_{kk'}^{ll'}(q)\, \xi_j(q)}.$$

The weighted average of this expression is obtained exactly as in §1 by using Ott's formula. Performing the averaging process, the product in (2.26′), which is the only part affected, becomes

(2.29)
$$\prod_j \prod_q{}' \, e^{-\left\{\left(M_{kk'}^{ll'}(j,q)\right)^2 + \left(N_{kk'}^{ll'}(j,q)\right)^2\right\} \frac{\hbar}{4\omega_j(q)} \coth \frac{\beta_j(q)}{2}},$$

$$\beta_j(q) = \frac{\hbar\,\omega_j(q)}{kT}.$$

The quantity $\left(M_{kk'}^{ll'}(j,q)\right)^2 + \left(N_{kk'}^{ll'}(j,q)\right)^2$ can be written down immediately from (2.28)

Thus :-

(2.30)
$$V_{kk'} = \frac{1}{2}\left\{\left(M_{kk'}^{ll'}(j,q)\right)^2 + \left(N_{kk'}^{ll'}(j,q)\right)^2\right\}.$$

$$\therefore \; V_{kk'}^{ll'}(j,q) = \frac{1}{N} \left| L_k^j(q)\, e^{i(l,q)} - L_{k'}^j(q)\, e^{i(l',q)} \right|^2$$

$$(2.30) \qquad = \frac{1}{N} \left[|L_k^j(q)|^2 + |L_{k'}^j(q)|^2 - \left\{ L_k^j(q)\, L_{k'}^{*j}(q)\, e^{i(l-l',q)} + L_k^{*j}(q)\, L_{k'}^j(q)\, e^{-i(l-l',q)} \right\} \right]$$

Thus $V_{kk'}^{ll'}(j,q)$ is a real quantity, and since

$$\left\{ L_k^j(q)\, e^{i(l,q)} - L_{k'}^j(q)\, e^{i(l',q)} \right\} = \left\{ L_k^j(-q)\, e^{i(l,-q)} - L_{k'}^j(-q)\, e^{i(l',-q)} \right\},$$

the expression for $V_{kk'}^{ll'}(j,q)$ is an even function of q. Also from the first form in which it has been written, we see that it is a positive quantity. Thus the infinite product in (2.29) can again be extended over the whole of q-space, a factor $\frac{1}{2}$ being added in the exponent. Thus the product becomes

$$(2.31) \qquad e^{-\sum_j \sum_q V_{kk'}^{ll'}(j,q) \frac{\hbar}{4\omega_j(q)} \coth \frac{\beta_j(q)}{2}} = e^{-V_{kk'}^{ll'}},$$

where

$$(2.32) \qquad V_{kk'}^{ll'} = \sum_j \sum_q V_{kk'}^{ll'}(j,q) \frac{\hbar}{4\omega_j(q)} \coth \frac{\beta_j(q)}{2}.$$

When the number of cells in the crystal becomes large, the difference between consecutive values of each of the q_α, $(\alpha = 1,2,3)$ becomes small, $\frac{2\pi}{n}$, and the summation over q can be replaced by an integral. Thus for a regular function $F(q_1, q_2, q_3)$

$$\sum_{q_1 q_2 q_3} F(q_1, q_2, q_3) = \left(\frac{n}{2\pi}\right)^3 \iiint_{-\pi}^{\pi} F(q_1, q_2, q_3)\, d\bar{q}.$$

$$d\bar{q} = dq_1\, dq_2\, dq_3\,., \qquad n^3 = N.$$

Thus proceeding to the limit for large N, $V_{kk'}^{ll'}$ can be written in the form

$$(2.34) \qquad V_{kk'}^{ll'} = \sum_j \int_{-\pi}^{\pi} V_{kk'}^{ll'}(j, q)\, \frac{\hbar}{4\omega_j(q)} \coth \frac{\beta_j(q)}{2}\, d\bar{q}$$

$$= U_k + U_{k'} - U_{kk'}^{ll'}.$$

where

$$(2.35) \qquad \begin{cases} U_k = \dfrac{1}{(2\pi)^3} \displaystyle\sum_j \int_{-\pi}^{\pi} |L_k^j(q)|^2 \frac{\hbar}{4\omega_j(q)} \coth \frac{\beta_j(q)}{2}\, d\bar{q}. \\ U_{kk'}^{ll'} = \dfrac{1}{(2\pi)^3} \displaystyle\sum_j \int_{-\pi}^{\pi} \left[L_k^j(q)\, L_{k'}^{*j}(q)\, e^{i(l-l', q)} + L_k^{*j}(q)\, L_{k'}^j(q)\, e^{-i(l-l', q)} \right] \frac{\hbar \coth \frac{\beta_j(q)}{2}}{4\omega_j(q)}\, d\bar{q} \end{cases}$$

Actually when the vibration $\omega_j(q)$ is one of those in the acoustical branch the origin in q -space must be excluded from the domain of integration, since, corresponding to $q = 0$ we would have $\omega_j(q) = 0$ i.e. the lattice vibrations correspond to a translation of the crystal as a whole. For the same reasons as in §1 this must be omitted.

Introducing all these results in the weighted average $\sum_n |f|^2(n, n)\, W(n)$ of $|f|^2$ we obtain

$$(2.36) \qquad \sum_n |f|^2(n, n)\, W(n) = \sum_{kk'} A_k A_{k'}^{*}\, e^{-(U_k + U_{k'})} \mathop{S}_{ll'} e^{i(l-l', q)}\, e^{U_{kk'}^{ll'}}.$$

We shall now consider the order of magnitude of $U_{kk'}^{ll'}$ with a view to expanding the exponential function $e^{U_{kk'}^{ll'}}$ in a series. Writing the integrand of the expression (2·35) for $U_{kk'}^{ll'}$, in extenso, it is

$$(2.37) \quad \sum_{xy}\sum_{j}\left[\left(\frac{2\pi}{\lambda}\right)^2 \frac{(s-s')_x(s-s')_y}{\sqrt{m_k m_{k'}}}\left\{ e^j_{kx}(q)\, e^{*j}_{k'y}(q)\, e^{i(l-l',q)} + e^{*j}_{kx}(q)\, e^j_{k'y}(q)\, e^{-i(l-l',q)}\right\} \frac{\hbar}{4\omega_j(q)} \coth\left(\frac{\hbar\omega_j}{2kT}\right.\right.$$

Since for all branches j of the lattice vibrations the components of the eigen-vectors $\underline{e}^j_k(q)$ assume finite values, which on account of the normalising equations (2·10) are of modulus not greater than unity

$$\left| e^j_{kx}(q)\, e^{*j}_{k'y}(q)\, e^{i(l-l',q)} \right| \leq 1,$$

and thus

$$\left| e^j_{kx}(q)\, e^{*j}_{k'y}(q)\, e^{i(l-l',q)} + e^{*j}_{kx}(q)\, e^j_{k'y}(q)\, e^{-i(l-l',q)} \right| \leq 2,$$

and the expression (2·37) is less than

$$2 \cdot \left(\frac{2\pi}{\lambda}\right)^2 \cdot 2(1-\cos\theta) \cdot \frac{1}{\sqrt{m_k m_{k'}}} \sum_j \frac{\hbar}{4\omega_j(q)} \coth\frac{\hbar\omega_j(q)}{2kT},$$

θ is the angle of scattering.

and, by the maximum modulus theorem, the modulus of the integral in the expression for $U_{kk'}^{ll'}$ is less than

$$(2.38) \quad \frac{4(1-\cos\theta)}{\sqrt{m_k m_{k'}}} \left(\frac{2\pi}{\lambda}\right)^2 \sum_j \int_{-\pi}^{\pi} \frac{\hbar}{4\omega_j(q)} \coth\left(\frac{\hbar\omega_j(q)}{2kT}\right) . \, d\bar{q}$$

Assuming T does not become very large, (which is a reasonable assumption, since this theory deals only with crystal structure, and at very high temperatures the substance will begin to lose this form), the only parts of this expression which would give rise to singularities are those parts for which ω_j belongs to the acoustical branch of the vibrations and q lies in the neighbourhood of the origin. The actual origin itself must be excluded, as has already been stated. To find the contribution to the integral which the acoustical vibrations $\omega_1, \omega_2, \omega_3$ for small q make, we consider the value of

$$(2.39) \qquad \sum_{j=1}^{3} \int \frac{\hbar}{4\omega_j(q)} \coth \frac{\hbar\omega_j(q)}{2kT} \cdot d\bar{q},$$

where the integral is taken over a small sphere of radius q_0 drawn about the origin. The volume element $d\bar{q}$ can then be replaced by $q^2 \sin\theta \, dq \, d\theta \, d\phi$.

In this region $\omega_j^2(q)$, $j=1,2,3$ is of the form,

$$\omega_j^2(q) = c_j^2 q^2$$

c_1, c_2, c_3 are the velocities of sound in the directions of the axes.

and $\coth \dfrac{\hbar\omega_j(q)}{2kT}$ can be expanded in a power series of $\omega_j(q)$.

$$\coth \frac{\hbar\omega_j(q)}{2kT} = \frac{2kT}{\hbar\omega_j(q)} \left\{ 1 + \frac{1}{3} \frac{\hbar^2 \omega_j^2(q)}{4k^2T^2} + \cdots \right\} \rightarrow \frac{2kT}{\hbar c_j q},$$

provided $\hbar\omega_j(q) < 2kT$.

Thus the expression (2·39) behaves like

$$\sum_{j=1}^{3} \int_0^{q_0} \int_0^{\pi} \int_0^{2\pi} \frac{kT}{c_j^2 q^2} \, q^2 \sin\theta \, dq \, d\theta \, d\varphi = 4\pi q_0 kT \sum_{j=1}^{3} \left(\frac{1}{c_j^2}\right).$$

the terms which have been neglected being of the second and higher orders in q_0. This is small since q_0 is small, provided T does not become too large and thus $U_{kk'}^{ll'}$ has no singularity. The integral in (2·38) will in fact be bounded, and have some upper limit $M(T)$ which increases with T. If we introduce ω_0, the maximum frequency of the vibrational spectrum, and the Debye Temperature $\frac{\hbar}{k}\omega_0 = \Theta$ and write $\omega_j(q) = \omega_0 W_j(q)$. then we see that the expression (2·38) is

$$\frac{4(1-\cos\theta)}{\sqrt{m_k m_{k'}}} \left(\frac{2\pi}{\lambda}\right)^2 \frac{\hbar^2}{k.\Theta} \sum_j \int_{-\pi}^{\pi} \frac{1}{W_j(q)} \coth\left(\frac{\Theta}{2T} \cdot W_j(q)\right) d\bar{q},$$

where $0 \leq W_j(q) \leq 1$. For substances which are hard Θ is high, and so the factor $\frac{\Theta}{T}$ is not small unless experiments are carried out at high temperatures, which is not the case. Thus the integral is finite, and the factor multiplying it must be small. This factor can be written

$$\frac{8(1-\cos\theta)}{\Theta\sqrt{\mu_k \mu_{k'}}} \cdot \frac{1}{\lambda^2} \cdot b.$$

where μ_k = the atomic weight of the atom

and
$$b = \frac{h^2}{2m_H k} = (957) \deg K,$$

if λ is measured in A.U.

Thus the constant factor is small if $\mu_K, \mu_{K'}$ are large, Θ is large, directions not far removed from the incident beam are considered and λ is large. However λ is restricted also by the fact that in order to obtain Laue spots at all it must be smaller than the distances between particles of the lattice.

If we take the special case of diamond as an example $\Theta = 2340\,^\circ K$ and $\mu_K = \mu_{K'} = 12$, so the numerical factor we are considering is

$$\frac{8(1-\cos\theta)}{\lambda^2} \cdot \frac{957}{12 \cdot 2340}$$

a value of λ used by Bragg is about 0.7 A.U., thus this constant $= 0.56(1-\cos\theta)$ which is small for small θ.

Thus $U_{KK'}^{ll'}$ does not have any singularities and can be made small. We shall assume that Θ, m_K, $m_{K'}$ and λ are chosen suitably to make it possible to expand $e^{U_{KK'}^{ll'}}$ in a power series and neglect terms of second and higher orders. Thus we assume in the expression (2·36) that the double sum over l and l' approximates to

$$\underset{ll'}{S}\; e^{i(l-l',\varphi)} \left\{ 1 + U_{KK'}^{ll'} + \cdots \right\}$$

Now

$$(2.38) \qquad \underset{ll'}{S}\; e^{i(l-l',\varphi)} = \left| \underset{l_1 l_2 l_3}{S}\; e^{i(l_1\varphi_1 + l_2\varphi_2 + l_3\varphi_3)} \right|^2 = \prod_{\alpha=1}^{3} \left(\frac{\sin \frac{n\varphi_\alpha}{2}}{\sin \frac{\varphi_\alpha}{2}} \right)^2 = 2\pi^3 N . \delta_N(\varphi_\alpha).$$

where

$$\delta_N(\varphi) = \delta_n(\varphi_1)\,\delta_n(\varphi_2)\,\delta_n(\varphi_3),$$

and is the Laue intensity factor. As $n \to \infty$ each of the $\delta_n(Q_\alpha)$ approaches the periodic Dirac delta function $\delta(Q_\alpha)$, which is of period 2π, and has singularities at $Q_\alpha = 2\pi k_\alpha$, k_α an integer. We shall assume that the crystal is large enough to replace $\delta_n(Q_\alpha)$ by $\delta(Q_\alpha)$. Then we have

(2.39) $$\underset{ll'}{S}\, e^{i(l-l',Q)} = 2\pi^3 N\, \delta(Q_1)\,\delta(Q_2)\,\delta(Q_3) = 2\pi^3 N\, \delta(Q).$$

and

$$\underset{ll'}{S}\, e^{i(l-l',Q)}\, U_{kk'}^{ll'} = N \sum_j \int_{-\pi}^{\pi} d\bar{q} \left[L_k^j(q)\, L_{k'}^{*j}(q)\, \delta(q+Q) + L_k^{*j}(q)\, L_{k'}^j(q)\, \delta(q-Q) \right] \frac{\hbar}{4\omega_j(q)} \coth\frac{\beta_j(q)}{2}$$

(2.40) $$= N \sum_j \left[L_k^j(-\bar{Q})\, L_{k'}^{*j}(-\bar{Q}) + L_k^j(\bar{Q})\, L_{k'}^j(\bar{Q}) \right] \frac{\hbar}{4\omega_j(\bar{Q})} \coth\frac{\beta_j(\bar{Q})}{2}$$

(2.40') $$= N \sum_j \left[L_k^{*j}(\bar{Q})\, L_{k'}^j(\bar{Q}) \right] \frac{\hbar}{2\omega_j(\bar{Q})} \coth\frac{\beta_j(\bar{Q})}{2}.$$

where $\bar{Q}$ means we must take the reduced value of i.e. if $2\pi k_\alpha \leq Q_\alpha < 2\pi(k_\alpha+1)$.

(2.41) $$\bar{Q}_\alpha = Q_\alpha - 2\pi k_\alpha.$$

Thus $I = I_0 C \sum_n |f|^2 (n,n)\, W(n)$ is split up into two parts

$$I = I_L + I_B ,$$

where

(2.42) $$I_L = I_0\, C N\, (2\pi)^3\, \delta(Q) \sum_{kk'} A_k A_{k'}^*\, e^{-(U_k + U_{k'})},$$

and represents the Laue Scattering. This quantity is everywhere small, except at $\varphi_\alpha = 2\pi K_\alpha$ ($\alpha = 1,2,3$; K_α integers) where it has sharp maxima - giving the Laue spots. These are the well-known equations for a Bragg reflexion,

$$(\underline{K}' - \underline{K})\, \underline{a}_\alpha = 2\pi K_\alpha ,$$

which may also be written

$$(2.43) \qquad \underline{K}' - \underline{K} = 2\pi \underline{b}_K ,$$

where $\underline{b}_K$ is the point $K_1\underline{b}_1 + K_2\underline{b}_2 + K_3\underline{b}_3$ of the reciprocal lattice.

Putting this value of $(\underline{K}' - \underline{K})$ in U_k, we get the value for the intensity of the Laue spot.

$$(2.44) \qquad \begin{aligned} I_L &= I_0 CN\ \delta(\varphi)(2\pi)^3 \sum_{kk'} g_k g_{k'}\, e^{-2\pi i (\underline{b}_K \cdot \underline{r}_k - \underline{r}_{k'})} \\ &= I_0 CN (2\pi)^3\, \delta\varphi \sum_{kk'} g_k g_{k'} \cos 2\pi \left(\underline{b}_K \cdot \underline{r}_k - \underline{r}_{k'}\right), \end{aligned}$$

where

$$g_k = f_k e^{-U_k}, \qquad \text{and is real, since } f_k$$

and U_k are real.

The expression for the background scattering I_B is

$$\begin{aligned} I_B &= I_0 CN \sum_{kk'} \sum_j A_k A^*_{k'}\, e^{-(U_k + U_{k'})} \left\{ L^{*j}_k(\bar{\varphi})\, L^j_{k'}(\bar{\varphi}) \right\} \frac{\hbar}{2\omega_j(\bar{\varphi})} \coth \frac{\beta_j(\bar{\varphi})}{2} \\ &= I_0 CN \sum_{kk'} \sum_j g_k g_{k'} \left[L^{*j}_k(\bar{\varphi})\, L^j_{k'}(\bar{\varphi})\, e^{-\frac{2\pi i}{\lambda}(\underline{s} - \underline{s}' \cdot \underline{r}_k - \underline{r}_{k'})} \right] \frac{\hbar}{2\omega_j(\bar{\varphi})} \coth \frac{\beta_j(\bar{\varphi})}{2} \\ &= I_0 CN \sum_{kk'} \sum_j g_k g_{k'} \left\{ B_{kk'}(\bar{\varphi}) \cos 2\pi (\underline{s} - \underline{s}' \cdot \underline{r}_k - \underline{r}_{k'}) + i\, C_{kk'}(\bar{\varphi}) \sin 2\pi (\underline{s} - \underline{s}' \cdot \underline{r}_k - \underline{r}_{k'}) \right\}. \end{aligned}$$

where

$$(2.46) \quad \begin{cases} B_{kk'}(q) = \sum_j \left\{ L_k^j(q)\, L_{k'}^{*j}(q) + L_k^{*j}(q)\, L_{k'}^j(q) \right\} \dfrac{\hbar}{4\omega_j(q)} \coth \dfrac{\beta_j(q)}{2} \\[2ex] C_{kk'}(q) = \sum_j \left\{ L_k^j(q)\, L_{k'}^{*j}(q) - L_k^{*j}(q)\, L_{k'}^j(q) \right\} \dfrac{\hbar}{4\omega_j(q)} \coth \dfrac{\beta_j(q)}{2} \end{cases} .$$

<u>Temperature effect on Background and Laue Scattering.</u>

It has been stated in an article by Preston (Nature 147. p 467.), referring to the work of Mrs. Lonsdale, that the extra spots in the Laue photograph appear in the neighbourhood of a Laue spot, when the crystal is turned through a <u>small</u> angle from the position giving the Bragg reflexion. As it is these extra spots that interest us, we shall consider only the value of I_B in the neighbourhood of a Laue spot, for a setting of the crystal only slightly removed from that which gives rise to a Laue spot. This amounts to treating small values of $\bar{\varphi}$.

We shall first consider the effect which the optical and acoustical branches of the lattice vibration have upon the extra spots. As $q \to 0$ each of the eigen-vectors $\underline{e}^j_k(q)$ approaches some non-zero value. The frequencies for the optical branches of the vibrations which we shall call $\omega_4, \omega_5 \cdots \omega_{3s}$ can be expanded in the form

$$\omega_j^0 + \omega_j^{(2)} q^2 + \cdots \qquad , \quad q^2 = q_1^2 + q_2^2 + q_3^2 ,$$

where ω_j^0 are not zero. Thus we see that, in the neighbourhood of $q = 0$, $\dfrac{1}{\omega_j(q)}$ and $\coth \dfrac{\hbar\omega_j(q)}{2kT}$ (for $j = 4 \cdots 3s$) are finite steadily varying functions of q.

Thus the terms

$$\sum_{j=4}^{3s} \left\{ L^j_k(\bar{\varphi})\, L^{*j}_{k'}(\bar{\varphi}) + L^{*j}_k(\bar{\varphi})\, L^j_{k'}(\bar{\varphi}) \right\} \frac{\hbar}{4\,\omega_j(\bar{\varphi})} \coth \frac{\beta_j(\bar{\varphi})}{2} ,$$

and

$$\sum_{j=4}^{3s} \left\{ L_k^j(\bar{q})\, L_{k'}^{xj}(\bar{q}) - L_k^{xj}(\bar{q})\, L_{k'}^j(\bar{q}) \right\} \frac{\hbar}{4\omega_j(\bar{q})} \coth \frac{\beta_j(\bar{q})}{2} ,$$

appearing in I_B, will contribute only a smooth intensity, and cannot give rise to any spots in the neighbourhood of the Laue spots, since there they assume almost constant values.

However, a fact we have already used in the neighbourhood of $q=0$, the three acoustical branches of the vibrations, $\omega_1, \omega_2, \omega_3$ have the expansions

$$\omega_j(q) = c_j . q + \cdots ,$$

and

$$\coth \frac{\beta_j(q)}{2} \to \frac{2kT}{\hbar\omega_j(q)} . \qquad \therefore \frac{1}{\omega_j(q)} \coth \frac{\beta_j(q)}{2} = O(1/q^2).$$

Thus the greatest contribution to I_B arises from this branch of the vibrations. Also any fluctuations in q, although they may be small, will produce comparatively large fluctuations in $\frac{1}{q^2}$, and thus there is a possibility of obtaining fairly well defined spots. Consequently we shall consider only the contributions to I_B arising from the acoustical branches of the vibrations $\omega_1, \omega_2, \omega_3$.

It is well known in the theory of lattice vibrations, that as a first approximation, for small q, the eigen vectors, $\underline{e}_k^j(q)$, $(j=1,2,3)$ approach a constant value for all k, i.e. $\underline{e}^j(q)$ say. Thus to the first approximation $B_{kk'}$ and $C_{kk'}$ approach values independent of k and k' except for a factor $\frac{1}{\sqrt{m_k m_{k'}}}$ namely

$$(3.1)\quad \begin{cases} B_{kk'}(q) \to \frac{1}{\sqrt{m_k m_{k'}}} \sum_{j=1}^{3} |L^j(q)|^2 \frac{\hbar}{2\omega_j(q)} \coth \frac{\beta_j(q)}{2}. \\ \\ C_{kk'}(q) \to 0. \end{cases}$$

$$L^j(q) = \left(\underline{K} - \underline{K}' \cdot \underline{e}_j(q)\right).$$

To the same approximation everywhere where $\frac{2\pi}{\lambda}(\underline{s}-\underline{s}')$ appears in I_B it may be replaced by its value, at the corresponding Laue spot, i.e. $2\pi b_K$.

$$I_B = I_0 CN \sum_{kk'} \left(\frac{g_k g_{k'} \cos 2\pi(\underline{b}_K \cdot \underline{r}_k - \underline{r}_{k'})}{\sqrt{m_k m_{k'}}} \right) \sum_{j=1}^{3} \left(|L^j(\bar{\varphi})|^2 \frac{\hbar}{2\omega_j(\bar{\varphi})} \coth \frac{\beta_j(\bar{\varphi})}{2} \right)$$

$$\sim I_0 CN \sum_{kk'} \frac{g_k g_{k'} \cos 2\pi(\underline{b}_K \cdot \underline{r}_k - \underline{r}_{k'})}{\sqrt{m_k m_{k'}}} \sum_{j=1}^{3} |L^j(\bar{\varphi})|^2 \frac{kT}{c_j^2 \bar{\varphi}^2}.$$

We shall write down beside this, for sake of comparison, the expression I_L .

$$I_L = I_0 CN \sum_{kk'} \frac{g_k g_{k'} \cos 2\pi(\underline{b}_K \cdot \underline{r}_k - \underline{r}_{k'})}{\sqrt{m_k m_{k'}}} (2\pi)^3 \delta(\varphi).$$

It is easily seen that the background intensity in the neighbourhood of a Laue spot and, as a consequence, that of any extra spots, is proportional to the intensity of the Laue spot.

We shall consider how temperature affects the intensities I_L, I_B respectively. The temperature factor in I_L appears only in the term $g_k g_{k'}$, it is in fact $e^{-(U_k + U_{k'})}$, where

$$U_k = \frac{1}{(2\pi)^3} \sum_{j=1}^{3s} \int_{-\pi}^{\pi} |L_k^j(q)|^2 \frac{\hbar}{4\omega_j(q)} \coth\left(\frac{\hbar\omega_j(q)}{2kT}\right) dq.$$

U_k is a positive increasing function of .
Consequently $e^{-(U_k+U_{k'})}$ decreases as T increases, i.e. the Laue spots are brighter at low temperatures than at high. Photographs obtained by Mrs. Lonsdale for experiments at liquid air temperature and at room temperature bring out this fact very clearly. (Nature 147, p. 467).

The part of I_B which depends on temperature is $y(T) = Te^{-(U_k+U_{k'})}$. This vanishes for zero temperature - i.e. at low temperatures the extra spots vanish. This is in agreement with experiment. As T increases $y(T)$ also increases, until it reaches a maximum value, and then it decreases again and $\to 0$ as $T \to \infty$. This final decrease has not been observed experimentally. The temperature at which it will begin depends on the magnitude of U_k and is higher the smaller U_k is. If U_k is small, which, by considerations, similar to those made when the validity of expanding $e^{U^{ll'}_{kk'}}$ in a series was being investigated, we expect that U_k will be small, and consequently the temperature at which there ~~is~~ the maximum is large.

In passing we shall consider how I_B is affected by the physical properties of the substance under investigation.

$$I_B = I_0 CN \left\{ \sum_{kk'} g_k g_{k'} \cos 2\pi \left(\underline{b}_k . \underline{r}_k - \underline{r}_{k'} \right) \right\} \frac{h^2}{k\Theta} \left(\frac{2\pi}{\lambda}\right)^2 \frac{1}{\sqrt{m_k m_{k'}}} \sum_{j=1}^{3} \left| L_j(\bar{\varphi}) \right|^2 \frac{\coth \frac{\Theta w_j(\bar{\varphi})}{2T}}{2 w_j(\bar{\varphi})}$$

Thus the intensity decreases with increase of the wave length of the incident X-Ray, weights of the atoms in these substances, and also the Debye temperature. For the convergence of our theory these quantities must have definite lower limits.

Background scattering for diagonal lattices.

We shall consider in this section the positions of the extra-spots for crystals which have three perpendicular axes of symmetry, Ox, Oy, Oz and allow the group of transformations

$$(x,y,z), \quad (x,-y,-z), \quad (-x,y,-z), \quad (-x,-y,z).$$

as well as a cyclic interchange of (x,y,z). (Diagonal Lattices, Born. 1923, §13). For such lattices all the particles must lie at the vertices of cubes having sides in the directions Ox, Oy, Oz or on the diagonals of the cubes. Four well-known lattice types which fall into this group are the simple, face-centred and body-centred cubic, and the diamond. For the first three the smallest cell contains one particle only, and has its sides defined by the vectors ($\underline{a}_1, \underline{a}_2, \underline{a}_3$) which will be given presently in terms of the vectors $\underline{i}, \underline{j}, \underline{k}$ along the sides of the cubic cell i.e. along Ox, Oy, Oz. For the diamond lattice the smallest cell contains two particles. In the theory we have worked out for the X-ray scattering, it is most convenient to deal with the smallest cells, so that in the sums (2·39), (2·40) taken over l all integral values of l are included, and thus the Delta functions arise immediately, without any algebraic manipulation. Taking the face-centred lattice as an example, it is easily seen how complications would have arisen had the lattice been referred to the cubic cell, for then the position of a particle is given by ($l_1\underline{i} + l_2\underline{j} + l_3\underline{k}$) where l_1, l_2, l_3 are restricted so that $l_1+l_2+l_3$ is always even. However, in considering the positions of the extra spots it is much more convenient to refer the lattice to the cubic cell.

We call the sides of the cubic cell $2a$. Then for the four particular lattices mentioned, (and we shall consider only these types, as the substances examined are of such structures) the vectors defining the smallest cell are

Simple $\underline{a}_1 = 2a.\underline{i}$, $\underline{a}_2 = 2a\,\underline{j}$, $a_3 = 2a.\underline{k}$.

(4.1) Face centred and Diamond $\underline{a}_1 = a(\underline{j}+\underline{k})$, $\underline{a}_2 = a(\underline{k}+\underline{i})$, $a_3 = a(\underline{i}+\underline{j})$.

Body centred $\underline{a}_1 = a(-\underline{i}+\underline{j}+\underline{k})$, $\underline{a}_2 = a(\underline{i}-\underline{j}+\underline{k})$, $\underline{a}_3 = a(\underline{i}+\underline{j}-\underline{k})$.

The second particle of the basis in the diamond lattice has the position vector

$$\tfrac{1}{2}a\,(\underline{i}+\underline{j}+\underline{k}) .$$

We shall denote by φ_α' the quantity $(\underline{K}'-\underline{K}\,.\,a_\alpha)$, $\alpha = 1,2,3$,

and by $\varphi_1 = 2\pi\,(\underline{K}'-\underline{K}).\underline{i}$, $\varphi_2 = 2\pi\,(\underline{K}'-\underline{K}).\underline{j}$, $\varphi_3 = 2\pi\,(\underline{K}'-\underline{K}).\underline{k}$. (4.2)

Then the conditions for a Bragg reflection are

$$\varphi_\alpha' = 2\pi K_\alpha' , \quad \alpha = 1,2,3 .$$

where K_α' are integers.

We shall find the corresponding relations for φ_α .

Using the equations above connecting $\underline{l}, \underline{j}, \underline{k}$ and $\underline{a}_1, \underline{a}_2, \underline{a}_3$, we obtain the following relations between φ_α and φ'_α.

(i) Simple lattice $\quad \varphi_\alpha = \varphi'_\alpha$.

(4.4) (ii) face-centred and diamond $\quad \varphi_1 = -\varphi'_1 + \varphi'_2 + \varphi'_3, \quad \varphi_2 = -\varphi'_2 + \varphi'_3 + \varphi'_1, \quad \varphi_3 = -\varphi'_3 + \varphi'_1 + \varphi'_2$.

(iii) body centred. $\quad \varphi_1 = \varphi'_2 + \varphi'_3, \quad \varphi_2 = \varphi'_3 + \varphi'_1, \quad \varphi_3 = \varphi'_1 + \varphi'_2$.

And the three corresponding conditions for a Bragg reflection are,

(i) $\quad \varphi_\alpha = 2\pi K_\alpha, \quad K_\alpha$ is any integer.

(ii) $\quad \varphi_1 = 2\pi(-K'_1 + K'_2 + K'_3), \quad \varphi_2 = 2\pi(K'_1 - K'_2 + K'_3), \quad \varphi_3 = 2\pi(K'_1 + K'_2 - K'_3)$.

or

(4.5) $\quad \varphi_\alpha = 2\pi K_\alpha$ where K_α are integers which must all be even or all odd.

(iii) $\quad \varphi_1 = 2\pi(K'_2 + K'_3), \quad \varphi_2 = 2\pi(K'_3 + K'_1), \quad \varphi_3 = 2\pi(K'_1 + K'_2)$.

i.e. $\quad \varphi_\alpha = 2\pi K_\alpha$ where K_α are integers restricted by $K_1 + K_2 + K_3$ must be even.

In the vibration equations it is most convenient to refer the eigen-vectors $\underline{e}^j_K(q)$ to the axes Ox, Oy, Oz i.e. sides of the cubic cell. Thus

$$L^j_K(q) = \frac{1}{\sqrt{m_K}} \left\{ (K-K')_x \, e^j_{Kx}(q) + (K-K')_y \, e^j_{Ky}(q) + (K-K')_z \, e^j_{Kz}(q) \right\},$$

where $(K-K')_z$ is the component of $(\underline{K}-\underline{K}')$ along Ox and thus

$$(4.6) \qquad (K-K')_x = (\underline{K}-\underline{K}' \cdot i) = \frac{\varphi_1}{2a}$$

Similarly

$$(K-K')_y = \varphi_2/2a \, , \qquad (K-K')_z = \varphi_3/2a$$

and consequently for a Bragg reflection

$$(K-K')_x = \frac{\pi K_1}{a}, \quad (K-K')_y = \frac{\pi K_2}{a}, \quad (K-K')_z = \frac{\pi K_3}{a}$$

The dynamical theory of diagonal lattices has been worked out in 'Atom theorie des Festen Zustandes', when the forces between particles are assumed to be central. The case of the diamond lattice where, as well as these forces there act also forces due to directed valency bonds has been worked out by Nagendra Nath. I have also developed the theory in a slightly different way, starting from a potential function, and have expressed the equations of the vibrations in terms of the three different elastic constants c_{11}, c_{12}, c_{44}. The results which we shall require to use in the following were found to hold equally well in the cases of central forces as in those forces which exist in the diamond.

It has already been stated that the greatest contribution to I_B is made by the acoustical branch of the vibrations, and the optical branch, in the vicinity of the Laue spot, can produce only a smooth, scattered intensity. Consequently in what follows we shall consider only the $\omega_j(q)$, $\underline{e}^j_k(q)$ corresponding to the acoustical branch of vibrations - and we shall restrict j to $1, 2, 3$. We also make use of the expansions of $\omega_j(q)$, $\underline{e}^j_k(q)$ given in

$$\omega_j^2(q) = c_j^2 q^2 + \cdots$$
$$\underline{e}^j_k(q) = \underline{e}_j + \underline{e}^{j,1}_k(q) + \cdots$$

The e_j are normalised by

$$\sum_j e^j_x e^j_y = \delta_{xy}$$

Then the values of c_j and $\underline{e}_j$ are given by the equations (Born 1923, p 648, (128''))

$$\rho c_j^2 e^j_x q^2 = \left[(c_{11}-c_{44})q_1^2 + c_{44}q^2\right] e^j_x + (c_{12}+c_{44})\, q_1 q_2 e^j_y + (c_{12}+c_{44})\, q_1 q_3 e^j_z \qquad (4.9)$$

c_{11}, c_{12}, c_{44} being the only three different, elastic constants which can exist for such a type of substance, and ρ is the density of matter. The eigen-vectors are referred to the cubic cell. The three values of c_j are the roots of the secular determinant of these equations.

To the approximation to which we are working the expression for $B_{kk'}$ is given by (3·1) and I_B by

$$I_B = I_0 CN \sum_{kk'} \frac{g_k g_{k'} \cos 2\pi (\underline{b}_K \cdot \underline{r}_k - \underline{r}_{k'})}{\sqrt{m_k m_{k'}}} \sum_{xy} (K-K')_x (K-K')_y \sum_{j=1}^{3} \frac{e^j_x(\bar{\varphi})\, e^j_y(\bar{\varphi})}{c_j^2\, \bar{\varphi}^2} \cdot kT \qquad (4.10)$$

This will have a maximum where

$$\sum_{xy} (K-K')_x (K-K')_y \sum_j \frac{e^j_x(\bar{\varphi})\, e^j_y(\bar{\varphi})}{c_j^2\, \bar{\varphi}^2} \qquad (4.11)$$

has a maximum.

Thus we require to find the quantities

$$(4.12) \qquad A_{xy} = \sum_j \frac{e_x^j(q)\, e_y^j(q)}{c_j^2 q^2} = A_{yx}.$$

This may be done by using the equations (5·9) and the ortho-normal properties of the $\underline{e}^j$. Each of the equations (5·9) is multiplied by $\underline{e}^j_{\bar{x}}/c_j^2 q^2$ and summation is made over j. Using the orthogonality conditions (5·3) we obtain immediately

$$(4.13) \qquad \left[(c_{11}-c_{44})q_1^2 + c_{44}q^2\right] A_{x\bar{x}} + (c_{12}+c_{44})\left(q_1q_2A_{y\bar{x}} + q_1q_3A_{z\bar{x}}\right) = \rho\,\delta_{x\bar{x}},$$

$$\bar{x} = x, y, z.$$

the remaining equations being obtained by cyclic interchange of x, y, z and a corresponding interchange of q_1, q_2, q_3.

This set of equations is consistent, and it is easily seen that the $A_{x\bar{x}}$ are ρ times the elements of the determinant which is inverse to

$$(4.14) \qquad \begin{vmatrix} (c_{11}-c_{44})q_1^2 + c_{44}q^2 & (c_{12}+c_{44})q_1q_2 & (c_{12}+c_{44})q_1q_3 \\ (c_{12}+c_{44})q_1q_2 & (c_{11}-c_{44})q_2^2 + c_{44}q^2 & (c_{12}+c_{44})q_2q_3 \\ (c_{12}+c_{44})q_1q_3 & (c_{12}+c_{44})q_2q_3 & (c_{11}-c_{44})q_3^2 + c_{44}q^2 \end{vmatrix}$$

For brevity we shall introduce ε, μ to represent the following combinations of the elastic constants

$$c_{11}-c_{12}-2c_{44} = \varepsilon, \qquad c_{12}+c_{44} = \mu \qquad \text{then} \quad c_{11}-c_{44} = \mu+\varepsilon.$$

Then

$$(4.15) \qquad \frac{A_{xx}}{\varepsilon(2\mu+\varepsilon)q_2^2q_3^2 - c_{44}(\mu+\varepsilon)q_1^2q^2 + c_{11}c_{44}q^4} = \frac{A_{yz}}{-\mu q_2q_3(\varepsilon q_1^2 + c_{44}q^2)}$$

$$= \frac{\rho}{\varepsilon^2(3\mu+\varepsilon)q_1^2q_2^2q_3^2 + \varepsilon(2\mu+\varepsilon)c_{44}q^2(q_2^2q_3^2+q_3^2q_1^2+q_1^2q_2^2) + c_{44}^2c_{11}q^6}$$

the other coefficients $A_{yy}, A_{zz} \ldots$ being obtained by a cyclic interchange of the co-ordinates x, y, z and a corresponding interchange of q_1, q_2, q_3.

Now for a perfectly isotropic substance ε is zero. We shall first determine the background intensity under the simplifying assumption that the anisotropy is negligible. For $\varepsilon = 0$, we obtain for the coefficients

$$(4.16) \qquad \frac{A_{xx}}{c_{11}q^2 - \mu q_1^2} = \frac{A_{yz}}{-\mu q_2 q_3} = \frac{\rho}{c_{11}c_{44}q^4} .$$

Thus the expression (4·11) becomes

$$\frac{\rho}{Aa^2}\left[\frac{c_{11}\,\bar{\varphi}^2\varphi^2 - \mu\left\{\varphi_1\bar{\varphi}_1 + \varphi_2\bar{\varphi}_2 + \varphi_3\bar{\varphi}_3\right\}^2}{c_{11}c_{44}\,\bar{\varphi}^4}\right],$$

where

$$\bar{\varphi}^2 = \left(\bar{\varphi}_1^2 + \bar{\varphi}_2^2 + \bar{\varphi}_3^2\right),$$

and

$$\varphi^2 = \varphi_1^2 + \varphi_2^2 + \varphi_3^2,$$

and $\qquad \varphi_1\bar{\varphi}_1 + \varphi_2\bar{\varphi}_2 + \varphi_3\bar{\varphi}_3 = \varphi \times$ the change in φ.

The expression (4·17) has an absolute maximum at $\bar{\varphi}_1 = \bar{\varphi}_2 = \bar{\varphi}_3 = 0$ i.e. at a Laue spot. For other small values of $\bar{\varphi}_1, \bar{\varphi}_2, \bar{\varphi}_3$ it is a positive monotonous decreasing function of $\bar{\varphi}_1, \bar{\varphi}_2, \bar{\varphi}_3$, ($c_{11} > \mu = c_{11} - c_{44}$, and $\varphi^2\bar{\varphi}^2 > \left(\varphi_1\bar{\varphi}_1 + \varphi_2\bar{\varphi}_2 + \varphi_3\bar{\varphi}_3\right)$)
Since the denominator is of the order $\bar{\varphi}^4$, and the numerator only of the order $\bar{\varphi}^2$, the fluctuations in the expression, since $\bar{\varphi}_1^2, \bar{\varphi}_2^2, \bar{\varphi}_3^2$ are small, will be influenced chiefly by the fluctuations of the denominator. Thus (4·17) and consequently I_B will have maxima when $\bar{\varphi}^2$, expressed in terms of the

small changes of the orientation of the crystal and the direction of the scattered intensity, has minimum values.

We shall consider the minimum values of $\tilde{\varphi}$ in the following case:-

We take the direction of the incident beam along the X-axis, fixed in space, and assume the crystal rotated about the Y-axis, which coincides with the y-axis of the crystal, perpendicular to it. The axes OX, OY, OZ fixed in space and Ox, Oy, Oz fixed in the crystal have the same origin. The setting of the crystal at any time is defined by ϕ the angle between Ox and OX.

The photographic plate is set up in a plane parallel to $X=0$

Referred to axes OX, OY, OZ, let the direction-cosines of the scattered intensity $\underline{s}'$ be ξ, η, ζ.

so that (4.18) $\cdot\cdot$ $\xi^2+\eta^2+\zeta^2=1$.

then we shall have

$$(4.19)\quad \begin{aligned} \varphi_1 &= 2a.\frac{2\pi}{\lambda}\left\{-(1-\xi)\cos\phi+\zeta\sin\phi\right\} \\ \varphi_2 &= 2a.\frac{2\pi}{\lambda}.\eta \\ \varphi_3 &= 2a.\frac{2\pi}{\lambda}\left\{(1-\xi)\sin\phi+\zeta\cos\phi\right\} \end{aligned}$$

A Laue spot is defined by giving these quantities three integral values k_1, k_2, k_3 $(\times 2\pi)$, which are to be restricted by equations (4·5). The equations (4·18), (4·19) give ξ_k, η_k, ζ_k and ϕ_k, for the Laue spot k_1, k_2, k_3.

$$(4{\cdot}20)\quad \begin{cases} \xi_\kappa = 1 - \frac{1}{8}\left(\frac{\lambda}{a}\right)^2 \kappa^2. \\ \eta_\kappa = \frac{\lambda}{a}\kappa_2 . \\ y_\kappa = \frac{\lambda}{2a}\sqrt{(\kappa^2-\kappa_2^2) - \frac{1}{16}\left(\frac{\lambda}{a}\right)^2 \kappa^4} . \\ \cos\phi_\kappa = \frac{1}{\kappa^2-\kappa_2^2}\left\{\kappa_3\sqrt{(\kappa^2-\kappa_2^2) - \frac{1}{16}\left(\frac{\lambda}{a}\right)^2\kappa^4} - \frac{1}{4}\left(\frac{\lambda}{a}\right)\kappa_1\kappa^2\right\}. \\ \sin\phi_\kappa = \frac{1}{\kappa^2-\kappa_2^2}\left\{\kappa_1\sqrt{(\kappa^2-\kappa_2^2) - \frac{1}{16}\left(\frac{\lambda}{a}\right)^2\kappa^4} - \frac{1}{4}\left(\frac{\lambda}{a}\right)\kappa_3\kappa^2\right\}. \end{cases}$$

In what follows we shall omit the suffix κ to the quantities ξ, η, y, ϕ although it must be understood that these have values corresponding to a Bragg reflexion. $\bar{Q}_\alpha$ is obtained from Q_α by giving ξ, η, y, ϕ small increments $\bar{\xi}, \bar{\eta}, \bar{y}, \bar{\phi}$. The direction-cosines of the scattered intensity being $\xi+\bar{\xi},\ \eta+\bar{\eta},\ y+\bar{y}$.

$$\therefore\quad (\xi+\bar{\xi})^2 + (\eta+\bar{\eta})^2 + (y+\bar{y})^2 = 1 .$$

and, by using (4·18)

$$(4{\cdot}21)\qquad \xi\bar{\xi} + \eta\bar{\eta} + y\bar{y} = -\tfrac{1}{2}(\bar{\xi}^2+\bar{\eta}^2+\bar{y}^2) \quad (= 0 \text{ to the first order}) .$$

The developments of $\bar{Q}_\alpha$ are then

$$(4{\cdot}22)\quad \begin{cases} \bar{Q}_1 = 2a.\frac{2\pi}{\lambda}\left[(\bar{\xi}\cos\phi + \bar{y}\sin\phi + ((1-\xi)\sin\phi + y\cos\phi)\bar{\phi} + \cdots\right]. \\ \bar{Q}_2 = 2a.\frac{2\pi}{\lambda}.\bar{\eta}. \\ \bar{Q}_3 = 2a.\frac{2\pi}{\lambda}\left[(-\bar{\xi}\sin\phi + \bar{y}\cos\phi - (-(1-\xi)\cos\phi + y\sin\phi)\bar{\phi} + \cdots\right]. \end{cases}$$

where $\bar{\xi}, \bar{\eta}, \bar{y}$ are connected by (4·21).

Maintaining first order terms only in $\bar{Q}_\alpha$ we get,

$$(4{\cdot}23)\quad \bar{Q}^2 = 4a^2\left(\frac{2\pi}{\lambda}\right)^2\left\{\bar{\xi}^2+\bar{\eta}^2+\bar{y}^2 + 2y\bar{\xi}\bar{\phi} + 2(1-\xi)\bar{y}\bar{\phi} + ((1-\xi)^2+y^2)\bar{\phi}^2 + \cdots\right].$$

$$= 4a^2\left(\frac{2\pi}{\lambda}\right)^2\left\{\frac{1-y^2}{\eta^2}\bar{\xi}^2 + \frac{1-\xi^2}{\eta^2}\bar{y}^2 + \frac{2y\xi}{\eta^2}\bar{\xi}\bar{y} + 2y\bar{\xi}\bar{\phi} + 2(1-\xi)\bar{y}\bar{\phi} + (2-2\xi-\eta^2)\bar{\phi}^2 + \cdots\right].$$

Considering $\bar{\xi}, \bar{\jmath}$ as independent coordinates this has minima where

$$\frac{\partial}{\partial \bar{\xi}} (\bar{\varphi}^2) = 0, \quad \text{ie} \quad \frac{1-y^2}{\eta^2}\bar{\xi} + \frac{y\xi}{\eta^2}\bar{\jmath} + y\bar{\Phi} = 0 .$$

(4.24)

$$\frac{\partial}{\partial \bar{\jmath}} (\bar{\varphi}^2) = 0, \quad \text{ie} \quad \frac{y\xi}{\eta^2}\bar{\xi} + \frac{1-\xi^2}{\eta^2}\bar{\jmath} + (1-\xi)\bar{\Phi} = 0 .$$

These have solutions

(4.25)

$$\bar{\xi} = -(1-\xi)\,y\,\bar{\Phi},$$

$$\bar{\jmath} = (y^2+\xi-1)\bar{\Phi},$$

and thus $\bar{\eta} = \eta y \bar{\Phi}.$

and these correspond to the positions of the extra spots.

It is of interest to express the position of the extra spot, however, not in terms of $\bar{\xi}, \bar{\eta}, \bar{\jmath}$ but in terms of χ the angle between the scattered intensity for the Laue spot and for the extra spot, and $\bar{\theta}$ the change in the angle which the scattered intensity makes with the incident beam.

Then

$$\cos\chi = \xi(\xi+\bar{\xi}) + \eta(\eta+\bar{\eta}) + y(y+\bar{\jmath})$$

$$= 1 + \xi\bar{\xi} + \eta\bar{\eta} + y\bar{\jmath} = 1 - \tfrac{1}{2}(\bar{\xi}^2+\bar{\eta}^2+\bar{\jmath}^2) \qquad \text{by (4.21)}$$

$$= 1 - \tfrac{1}{2}\left\{(1-\xi)^2y^2 + (y^2+\xi-1)^2 + \eta^2y^2\right\}\bar{\varphi}^2$$

$$= 1 - \tfrac{1}{2}(1-\xi)\bar{\Phi}^2.$$

Thus since χ is small , $\chi = (1-\xi)\,\bar{\Phi}$.

But

$$\xi = \cos\theta\,, \qquad \therefore \qquad (4{\cdot}26) \qquad \chi = 2\sin^2\theta/_2 \cdot \bar{\Phi}.$$

$$\text{and} \qquad \bar{\xi} = -\sin\theta.\,\bar{\theta} \;=\; -\,(1-\xi)\,y.\,\bar{\Phi}\,,$$

$$\therefore \quad \bar{\theta} = 2y\tan\theta/_2 \cdot \bar{\Phi}.$$

The expression obtained for χ is exactly that obtained by Jauncey (Nature $\underline{147}$. p 146) He started with a formula obtained by Bragg (Nature $\underline{146}$ p. 509), which was developed for K.Cl using Preston's idea that clusters of particles in the substance scattered independently. He assumed particles were situated at the corners of a cube. Raman's formula also approximates to this for small values of the angle between the directions of the intensity for the Laue and modified spots.

What we have done, virtually, is to neglect the term

$$\mu(\varphi_1\bar{\varphi}_1 + \varphi_2\bar{\varphi}_2 + \varphi_3\bar{\varphi}_3) \qquad \text{in } (4{\cdot}19).$$

Now

$$(\varphi_1\bar{\varphi}_1 + \varphi_2\bar{\varphi}_2 + \varphi_3\bar{\varphi}_3) = -\left(\frac{2\pi}{\lambda}\right)^2 4a^2\,\bar{\xi}.$$

Thus the exact value of (4•17) is

$$(4{\cdot}28) \qquad \frac{\rho}{4a^2}\left[\frac{c_{11}\left\{\frac{1-y^2}{\eta^2}\bar{\xi}^2 + \frac{1-\xi^2}{\eta^2}\bar{y}^2 + \frac{2y\xi}{\eta^2}\bar{y}\bar{\xi} + 2y\bar{\xi}\bar{\Phi} + 2(1-\xi)\bar{y}\bar{\Phi} + (2-2\xi-\eta^2)\bar{\Phi}^2\right\} - \mu\bar{\xi}^2}{c_{11}c_{44}\left\{\frac{1-y^2}{\eta^2}\bar{\xi}^2 + \frac{1-\xi^2}{\eta^2}\bar{y}^2 + \frac{2y\xi}{\eta^2}\bar{y}\bar{\xi} + 2y\bar{\xi}\bar{\Phi} + 2(1-\xi)\bar{y}\bar{\Phi} + (2-2\xi-\eta^2)\bar{\Phi}^2\right\}}\right].$$

The conditions for a maximum can be written in the following way,

(4.29) and
$$\begin{cases} \dfrac{1-\xi^2}{\eta^2}\,\bar{y} + \dfrac{\xi y}{\eta^2}\,\bar{\xi} + (1-\xi)\,\bar{\phi} = 0, \\[2ex] \left(A - \mu\dfrac{\bar{\xi}}{c_{11}}\right)B - 2A\left(B - \dfrac{\mu.\bar{\xi}^2}{c_{11}}\right) = 0, \end{cases}$$

where

(4.30)
$$A = \frac{1-y^2}{\eta^2}\,\bar{\xi} + \frac{y\xi}{\eta^2}\,\bar{y} + y\bar{\phi},$$

and

$$B = \frac{1-y^2}{\eta^2}\,\bar{\xi}^2 + \frac{1-\xi^2}{\eta^2}\,\bar{y}^2 + \frac{y\xi}{\eta^2}\,\bar{\xi}\bar{y} + 2y\bar{\xi}\bar{\phi} + 2(1-\xi)\,\bar{y}\bar{\phi} + (2-2\xi-\eta^2)\,\bar{\phi}^2,$$

this we shall write

$$= \left(\frac{1-y^2}{\eta^2}\bar{\xi} + \frac{y\xi}{\eta^2}\bar{y} + y\bar{\phi}\right)\bar{\xi} + \left(\frac{1-\xi^2}{\eta^2}\bar{y} + \frac{y\xi}{\eta^2}\bar{\xi} + (1-\xi)\bar{\phi}\right)\bar{y} + \left(y\bar{\xi} + (1-\xi)\bar{y} + (2-2\xi-\eta^2)\bar{\phi}\right)\bar{\phi}$$

Denote by $\bar{\xi}_0$, $\bar{y}_0$ the solutions of equations (4•24) which are given by (4•25) and let $\bar{\xi}_0 + \bar{\xi}_1$, $\bar{y}_0 + \bar{y}_1$ be solutions of (4•29). We shall work on the assumption that $\bar{\xi}_1$, $\bar{y}_1$ are small compared with $\bar{\xi}_0$, $\bar{y}_0$. Then in (4•29), as an approximation we retain only terms of the first order in $\bar{\xi}_1$, $\bar{y}_1$. If the resulting solution is small we shall know that the assumption is true and our approximation is valid.

Accordingly (4•29) became, using the expressions (4•25) for $\bar{\xi}_0$, $\bar{y}_1$

(4.32)
$$\frac{1-\xi^2}{\eta^2}\,\bar{y}_1 + \frac{y\xi}{\eta^2}\,\bar{\xi}_1 = 0,$$

and after some reduction

$$(4.33) \qquad \frac{\mu}{c_{11}}\left[\bar{\xi}_0\left\{\left(\frac{1-y^2}{\eta^2}\bar{\xi}_1 + \frac{y\xi}{\eta^2}\bar{\zeta}_1\right)\bar{\xi}_0 - \left(y\bar{\xi}_1 + (1-\xi)\bar{\zeta}_1\right)\bar{\phi}\right\} - y^2\phi^2\left(\bar{\xi}_0 + \bar{\xi}_1\right)\right]$$
$$- \left(\frac{1-y^2}{\eta^2}\bar{\xi}_1 + \frac{y\xi}{\eta^2}\bar{\zeta}_1\right) y^2\bar{\phi}^2 = 0$$

Eliminating $\bar{\zeta}_1$, by means of (4·32), $\bar{\xi}_1$ is given by

$$(4.34) \qquad \bar{\xi}_1\left[\frac{\mu}{c_{11}}\left[\left\{\frac{1-3\xi}{1+3\xi}\right\} - \frac{1}{1-\xi^2}\right]\right] = \frac{\mu}{c_{11}} \cdot y(1-\xi)\,\bar{\phi}$$

We see immediately that, for small θ, (θ is the angle of scattering) the most important term in the coefficient of $\bar{\xi}_1$ is $\frac{1}{1-\xi^2}$ and thus $\bar{\xi}_1$ is of the order of $y(1-\xi)^2$. This is θ^5 and is small compared with $\bar{\xi}_0$ which from (4·25) we see is of the order of magnitude of θ^3. Thus for small angles of scattering the additional term $\mu\bar{\xi}^2$ in the numerator only makes a small change in the position of the spot, this change since $\bar{\xi}_1$ is negative brings the extra spot nearer to the Laue spot.

We shall determine the values of χ and the shape of the extra spot when the term $\frac{\mu\bar{\xi}^2}{c_{11}}$ is taken into consideration in (4·14), assuming the approximation we have made is valid. The values of $\bar{\zeta}_1, \bar{\eta}_1$ corresponding to the solution found for $\bar{\xi}_1$ are

$$(4.35) \qquad \bar{\zeta}_1 = \frac{\mu}{c_{11}}\frac{y^2\xi(1-\xi)}{1-\frac{\mu}{c_{11}}(1-\xi)(1-3\xi)}, \qquad \bar{\eta}_1 = \frac{\mu}{c_{11}} \cdot \frac{\xi\eta y(1-\xi)}{1-\frac{\mu}{c_{11}}(1-\xi)(1-3\xi)}.$$

Thus the position of the extra spot is given by

$$
(4.36)\quad
\begin{cases}
\bar{\xi} = \left\{ -(1-\xi)\zeta - \dfrac{\mu}{c_{11}} \dfrac{\zeta(1-\xi)(1-\xi^2)}{1-\frac{\mu}{c_{11}}(1-\xi)(1-3\xi)} \right\} \bar{\phi} + \cdots \\[2ex]
\bar{\eta} = \left\{ \eta\zeta + \dfrac{\mu}{c_{11}} \dfrac{\xi\eta\zeta(1-\xi)}{1-\frac{\mu}{c_{11}}(1-\xi)(1-3\xi)} \right\} \bar{\phi} + \cdots \\[2ex]
\bar{\zeta} = \left\{ (\zeta^2+\xi-1) + \dfrac{\mu}{c_{11}} \dfrac{\zeta^2\xi(1-\xi)}{1-\frac{\mu}{c_{11}}(1-\xi)(1-3\xi)} \right\} \bar{\phi} + \cdots
\end{cases}
$$

and the value of χ is ,assuming θ is small and terms of θ^3 and higher orders can be neglected

$$
(4.37)\qquad \chi^2 = (1-\xi)^2\bar{\phi}^2 + \frac{2\mu}{c_{11}} \frac{\zeta^2\xi^2(1-\xi)^2}{1-\frac{\mu}{c_{11}}(1-\xi)(1-3\xi)} \bar{\phi}^2
$$

Thus we see that when the term $\frac{\mu}{c_{11}}\bar{\xi}^2$ in (4.17) is taken into account, the position of the extra spot depends not only on the value of ξ for the corresponding Laue spot but also on the athimuthal angle which appears in ζ, ie, for Laue spots lying on a circle about the incident beam the distance of the extra spot varies as we move round the circle. However the term in which ζ appears is small, of the fourth order in θ_1 and thus this effect is small.

The co-ordinates on the photographic plate, which we shall denote by (u,v) are, for small θ_1 to the first order proportional to η and ζ. Thus the curves of constant intensity in the neighbourhood of a Laue spot taking the Laue spot as origin, are, from (4.17)

$$\frac{B - \frac{\mu}{c_{11}}\left(\frac{\eta u + \gamma v}{\xi}\right)^2}{B^2} = C \qquad (4.38)$$

C is a constant, which must be less than the maximum value of the left-hand side.

where

$$B = \frac{1-\gamma^2}{\xi^2}u^2 + \frac{1-\eta^2}{\xi^2}v^2 + \frac{2\eta\gamma}{\xi}uv - \frac{2\eta\gamma}{\xi}u\bar{\Phi} + \frac{2(\eta^2+\xi-1)}{\xi}v\bar{\Phi} + (2-2\xi-\eta^2)\bar{\Phi}^2 \qquad (4.39)$$

When we make a change of co-ordinates corresponding to (a) a transformation of the origin to the centre of the extra spot (b) a rotation of the axes so that the new axes are along and perpendicular to the meridian through the Laue spot the equations of the curves of constant intensity become

$$\left(\frac{1}{\xi^2}U^2 + V^2 + \gamma^2\bar{\Phi}^2\right) - \frac{\mu}{c_{11}}\left(U + \gamma(\xi-\xi^2)\bar{\Phi}\right)^2 \frac{\eta^2+\gamma^2}{\xi^2} = C\left(V^2 + \frac{1}{\xi^2}U^2 + \gamma^2\bar{\Phi}^2\right)^2 \qquad (4.40)$$

The second term on the left-hand side has its coefficient of the second order in θ and thus is small compared with the other term. Thus as an approximation the curves of constant intensity are

$$\frac{1}{\xi^2}U^2 + V^2 + \gamma^2\bar{\Phi}^2 = \frac{1}{C} \qquad (4.41)$$

These are ellipses having their centres at the extra spot and minor and major axes in the ratio $\xi:1$. Since $\xi \approx 1$ the ellipticity is small

The exact curve of constant intensity is one of the fourth degree, which touches this ellipse where it is cut by

$$U + y(\xi - \xi^2)\bar{\Phi} = 0$$

Since the coefficient of the square of this linear expression is small, the fourth degree curve differs very little from the ellipse considered above. It can easily be shown to be closed, lie outside the ellipse and touch it near the end of the major axis.

The Positions of the extra spots in the case of anisotropy.

To determine the positions of the extra spots in the case of an anisotropic substance, even although the degree of anisotropy, which is measured by ε is small, becomes very complicated, since homogeneous equations of the ninth degree are involved. As a simplification we shall consider only reflections in the plane of the incident radiation which is perpendicular to the axis of rotation i.e. directions of scattering for which

$$\eta = 0 \quad \text{and also} \quad \bar{\eta} = 0,$$

the arrangement of the experiment being as described in the last section.

In such a case $\xi, \jmath$ and $\bar{\xi}, \bar{\jmath}$ can be expressed in terms of one parameter θ and its increment $\bar{\theta}$ only, where θ is the angle between the incident and scattered radiation for a Laue spot, and $\bar{\theta}$ is an angular deflection from the direction of the Laue spot.

In such a case we shall have,

$$(K-K')_y = 0 \ ,$$

so that the only quantities A_{xy} it is necessary to determine are A_{xx}, A_{zz} and A_{xz}. Before writing these we shall consider the expressions for Q_α and $\bar{Q}_\alpha$ in terms of θ, ϕ and $\bar{\theta}, \bar{\phi}$. Since

$$\xi = \cos\theta, \quad \jmath = \sin\theta \ ; \quad \bar{\xi} = -\sin\theta . \bar{\theta} \ , \quad \bar{\jmath} = \cos\theta . \bar{\theta} .$$

they are, using (4·19), (4·22)

$$(5.1) \qquad \begin{cases} Q_1 = \sigma\left(-\cos\phi + \cos(\phi - \theta)\right) \\ Q_2 = 0 \\ Q_3 = \sigma\left(\sin\phi - \sin(\phi - \theta)\right). \end{cases} \qquad \sigma = \frac{4\pi a}{\lambda}.$$

and

$$(5.2) \qquad \begin{cases} \bar{Q}_1 = \sigma\left(\bar{\theta}\sin(\phi - \theta) + 2\bar{\phi}\cos(\phi - \tfrac{\theta}{2})\sin\tfrac{\theta}{2}\right) \\ \bar{Q}_2 = 0 \\ \bar{Q}_3 = \sigma\left(\bar{\theta}\cos(\phi - \theta) - 2\bar{\phi}\sin(\phi - \theta/2)\sin\theta/2\right). \end{cases}$$

At the same time we shall write down certain combinations of the Q_α, $\bar{Q}_\alpha$ which will be required later,

$$\begin{cases} Q_1\bar{Q}_1 + Q_3\bar{Q}_3 = 2\sigma^2 \sin\theta/2 \cos\theta/2 \; \bar{\theta}. \\ Q_1\bar{Q}_3 - Q_3\bar{Q}_1 = 2\sigma^2(\bar{\theta} - 2\bar{\phi})\sin^2\theta/2. \\ \bar{Q}^2 = \sigma^2\left(\bar{\theta}^2 - 4\bar{\theta}\bar{\phi}\sin^2\theta/2 + 4\bar{\phi}^2\sin^2\theta/2\right) \\ \bar{Q}_1\bar{Q}_3 = \sigma^2\left[\tfrac{1}{2}\bar{\theta}^2\sin 2(\phi - \theta) + 2\bar{\theta}\bar{\phi}\cos\left(2\phi - \tfrac{3\theta}{2}\right)\sin\theta/2 - 2\bar{\phi}^2\sin(2\phi - \theta)\sin^2\theta/2\right]. \end{cases}$$

The quantities A_{xx}, A_{zz}, A_{xz} (4·15) are given by

$$(5.3) \qquad \frac{A_{xx}}{\bar{Q}_2\left(c_{11}c_{44}\bar{Q}^2 - c_{44}(c_{11} - c_{44})\bar{Q}_1^2\right)} = \frac{A_{zz}}{\bar{Q}^2\left(c_{11}c_{44}\bar{Q}^2 - c_{44}(c_{11} - c_{44})\bar{Q}_3^2\right)}$$

$$= \frac{A_{xz}}{-(c_{12} + c_{44})\,c_{44}\,\bar{Q}^2\bar{Q}_1\bar{Q}_3} = \frac{\rho}{c_{44}^2 c_{11}\bar{Q}^6 + c_{44}\,2.(c_{11} - c_{12})\,\bar{Q}^2\bar{Q}_1^2\bar{Q}_3^2}.$$

Writing in the denominators of A_{xx}, A_{zz}, $\bar{\varphi}^2 = \bar{\varphi}_1^2 + \bar{\varphi}_3^2$ we see they become $c_{44}\left(c_{11}\bar{\varphi}_3^2 + c_{44}\bar{\varphi}_1^2\right)$ and $c_{44}\bar{\varphi}^2\left(c_{11}\bar{\varphi}_1^2 + c_{44}\bar{\varphi}_3^2\right)$ respectively and the expression (4·11) of which we require the maximum becomes, apart from a factor ρ is

$$\frac{\varphi_1^2\left(c_{11}\bar{\varphi}_3^2 + c_{44}\bar{\varphi}_1^2\right) + \varphi_3^2\left(c_{11}\bar{\varphi}_1^2 + c_{44}\bar{\varphi}_3^2\right) - 2\varphi_1\varphi_3\left(c_{12}+c_{44}\right)\bar{\varphi}_1\bar{\varphi}_3}{c_{11}c_{44}\bar{\varphi}^4 + \varepsilon\left(c_{11}+c_{12}\right)\bar{\varphi}_1^2\bar{\varphi}_3^2}$$

$$= \frac{c_{11}\left(\varphi_1\bar{\varphi}_3 - \varphi_3\bar{\varphi}_1\right)^2 + c_{44}\left(\varphi_1\bar{\varphi}_1 + \varphi_3\bar{\varphi}_3\right) + 2\varepsilon\varphi_1\varphi_3\bar{\varphi}_1\bar{\varphi}_3}{c_{11}c_{44}\bar{\varphi}^4 + \varepsilon\left(c_{11}+c_{12}\right)\bar{\varphi}_1^2\bar{\varphi}_3^2} \tag{5.4}$$

This, expressed in terms of the quantities $\bar{\theta}, \bar{\phi}$ is,

$$\frac{\begin{aligned}4c_{11}\left(\bar{\theta}-2\bar{\phi}\right)^2\sin^4\tfrac{\theta}{2} + 4c_{44}\bar{\theta}^2\sin^2\tfrac{\theta}{2}\cos^2\tfrac{\theta}{2} + 4\varepsilon\sin\left(2\phi-\theta\right)\sin^2\tfrac{\theta}{2}\Big[\tfrac{1}{2}\bar{\theta}^2\sin 2(\phi-\theta) \\ + 2\bar{\theta}\bar{\phi}\cos\left(2\phi-\tfrac{3\theta}{2}\right)\sin\tfrac{\theta}{2} - 2\bar{\phi}^2\sin\left(2\phi-\theta\right)\sin^2\tfrac{\theta}{2}\Big]\end{aligned}}{\begin{aligned}c_{11}c_{44}\left[\bar{\theta}^2 - 4\bar{\theta}\bar{\phi}\sin^2\tfrac{\theta}{2} + 4\bar{\phi}^2\sin^2\tfrac{\theta}{2}\right]^2 + \varepsilon\left(c_{11}+c_{12}\right)\Big[\tfrac{1}{2}\bar{\theta}^2\sin 2(\phi-\theta) + 2\bar{\theta}\bar{\phi}\cos\left(2\phi-\tfrac{3\theta}{2}\right)\sin\tfrac{\theta}{2} \\ - 2\bar{\phi}^2\sin\left(2\phi-\theta\right)\sin^2\tfrac{\theta}{2}\Big]\end{aligned}} \tag{5.5}$$

This expression is still too general for a determination of the positions of the spots and a further simplification must be made. This will be, that we shall assume $\sin\frac{\theta}{2}$ is small, which just amounts to a consideration of the background scattering only in the neighbourhood of those Laue spots not far removed from the direction of the incident beam. This is what is actually done in experimental work and so the procedure is reasonable. The value of $\sin\frac{\theta}{2}$ is given by (4·20), for

$$\frac{\xi}{\xi} = \cos\theta = 1 - \frac{1}{8}\left(\frac{\lambda}{a}\right)^2 \kappa^2 \quad \text{and} \qquad \cos\theta = 1 - 2\sin^2\theta/_2 ,$$

$$\therefore \ \sin\frac{\theta}{2} = \frac{1}{4}\left(\frac{\lambda}{a}\right)\kappa .$$

since θ is small, and we assume

and as $\left(\frac{\lambda}{a}\right)$ must be chosen small, this is small for small κ. Thus, what we shall do virtually is to expand the value of $\bar{\theta}$ which gives $(5{\cdot}5)$ a minimum in powers of $\frac{\lambda}{a}$. We shall see immediately that two cases arise, according as one of κ_1 or κ_2 is or is not zero. In the first of these cases is either equal to $\frac{\theta}{2}$ or $\frac{\pi}{2}+\frac{\theta}{2}$, by $(5{\cdot}1)$. Both these values substituted in $(5{\cdot}5)$ give it the same value - this is to be expected since, on account of the symmetry of the crystal, they correspond to the same physical conditions. In the second case when neither κ_1 nor κ_2 is zero $\cos\phi$ and $\sin\phi$ can be expanded in power series in $\left(\frac{\lambda}{a}\right)$ each starting with a non-zero constant term, thus:-

$$(5{\cdot}6) \qquad \begin{aligned} \cos\phi &= \frac{\kappa_3}{\kappa} - \frac{1}{4}\left(\frac{\lambda}{a}\right)\kappa_1 - \frac{1}{32}\left(\frac{\lambda}{a}\right)^2 \kappa_3\kappa + \cdots , \\ \sin\phi &= \frac{\kappa_1}{\kappa} + \frac{1}{4}\left(\frac{\lambda}{a}\right)\kappa_3 - \frac{1}{32}\left(\frac{\lambda}{a}\right)^2 \kappa_1\kappa + \cdots . \end{aligned}$$

The two cases will be considered separately.

<u>(Case 1).</u> <u>Either κ_1 or κ_3 is zero.</u>

In this case $\phi = \frac{\theta}{2}$ or $\frac{\pi}{2}+\frac{\theta}{2}$ substituting this value in the expression $(5{\cdot}5)$, the terms arising from anisotropy vanish in the numerator, and the resulting quantity, which we write as $y(\bar{\theta})$ is

$$(5.7)\qquad y(\bar{\theta}) = \frac{4c_{11}(\bar{\theta}-2\bar{\Phi})\sin^4\theta/_2 + 4c_{44}\sin^2\theta/_2\cos^2\theta/_2\cdot\bar{\theta}^2}{c_{11}c_{44}\left[\bar{\theta}^2 - 4\bar{\theta}\bar{\Phi}\sin^2\frac{\theta}{2} + 4\bar{\Phi}^2\sin^4\frac{\theta}{2}\right] + \varepsilon(c_{11}+c_{12})\sin^2\frac{\theta}{2}\cos^2\frac{\theta}{2}(\bar{\theta}-2\bar{\Phi})^2}.$$

We assume that the value of $\bar{\theta}$ making this a maximum can be expanded in the form of a series in $\sin\frac{\theta}{2}$, thus

$$\bar{\theta} = \bar{\Phi}\left[a_0 + a_1\sin\frac{\theta}{2} + a_2\sin^2\frac{\theta}{2} + \dots\right].$$

If the maximum condition is written down, and only the lowest powers of $\sin\frac{\theta}{2}$ maintained, we obtain at first $a_0^5 = 0$. The equation for a_1 is

$$(5.8)\qquad 8c_{44}a_1\left[c_{11}c_{44}(a_1^2+4)^2 + 4\varepsilon(c_{11}+c_{12})a_1^2\right] - (16c_{11} + 4c_{44}a_1^2)\left(4c_{11}c_{44}(a_1^2+4) + 8\varepsilon(c_{11}+c_{12})\right)a_1 = 0.$$

This is, in fact, the coefficient of the lowest power of $\sin\frac{\theta}{2}$, (which is $\sin^4\frac{\theta}{2}$) in the numerator of $\frac{dy}{d\bar{\theta}}$. It has a root $a_1 = 0$, and as a_1, passes through these values $\frac{dy}{d\bar{\theta}}$ changes from positive to negative. Thus $a_1 = 0$ corresponds to a maximum of y. We shall not consider the other four non-zero roots of (5.8), since they will refer to positions in the plane at a greater distance from the Laue spot.

Proceeding in the same way we find the coefficient of the next higher order term in the numerator is (for $a_1 = 0$)

$$(5.9)\qquad (8c_{44}a_2 - 16c_{11})\,16c_{11}c_{44} - 16c_{11}\left(16c_{11}c_{44}(a_2-2) + 8\varepsilon(c_{11}+c_{12})a_2\right) = 0$$

$$\therefore\quad a_2 = \frac{-2c_{11}c_{44}}{c_{44}^2 - 2c_{44}c_{11} - \varepsilon(c_{11}+c_{12})} = \frac{+2c_{11}c_{44}}{2c_{11}c_{44} + \varepsilon(c_{11}+c_{12}) - c_{44}^2}$$

This is in general a ~~negative~~ positive quantity, although for special values of the elastic constants it could become positive. If it is negative or positive it corresponds to a maximum value of $y(\theta)$, since $\frac{dy}{d\theta}$ changes from positive to negative as a_2 passes through this value.

We shall consider the value in the special cases of Na and K.Cl.

NaCl $\qquad c_{11} = 4770, \quad c_{12} = 1299, \quad c_{44} = 1320.$ (in Kg/mm²)

By calculation we find $\quad a_2 = +0.65.$

K.Cl $\qquad c_{11} = 3750, \quad c_{12} = 655 \quad c_{44} = 198$

Then $\quad a_2 = +0.11.$

Thus the positions of the extra spots, to the lowest power of $\sin\frac{\theta}{2}$ appearing, are given by;-

NaCl; $\quad \bar{\theta} = +0.65 \sin^2\theta/2$; $\qquad$ KCl. $\bar{\theta} = +0.11 \sin^2\frac{\theta}{2}$.

These are of the same order of magnitude in $\sin\frac{\theta}{2}$ as predicted in other theories but numerical values of the constant factor, as predicted by our theory, differ.

I have been unable to obtain sufficient information about the elastic properties of diamond to determine the values of c_{11}, c_{12}, c_{44}. However, the values of these quantities have been determined theoretically by Nagendra Nath. He finds the relation

$$c_{11} \approx c_{12} + c_{44}$$

exists between the elastic constants. Now the quantity ($(c_{11} - c_{12} - c_{44})$) is a factor of the denominator of a_2 for we can write

$$a_2 = \frac{+\ 2c_{11}c_{44}}{(c_{11}-c_{12}-c_{44})\ (c_{11}+c_{12}+c_{44})} .$$

Thus for the diamond a_2 becomes very large. If the relation (5·10) is correct for the diamond, one of the roots of 5·8 other than $a_1 = 0$ must be considered. Then the deflection of the scattered radiation will be of the order of $\sin\frac{\theta}{2}\,\bar{\phi}$.

It is impossible to determine the exact shape of the extra spots from these considerations, as we have restricted ourselves to $\eta = 0$. The intensity of the spot can be calculated and involves the elastic constants in a complicated way. Thus it seems as if the behaviour of the extra spots depends largely on the elastic constants of the substance concerned, and no general formula determines their positions as in the case of the Laue spots.

We shall now consider the other case,

(<u>Case II</u>). $\kappa_1 \neq 0,\ \kappa_3 \neq 0$

Now we have to take (5·5) in the general form, and insert the expansions for $\cos\phi$ and $\sin\phi$ given by (5·6). The method of procedure is exactly the same as in case (1). We expand the value of $\bar{\theta}$, corresponding to the maximum of the expression (5·5) in a series,

$$\bar{\theta} = \bar{\phi}\,(a_0 + a_1 \sin\tfrac{\theta}{2} + \cdots) .$$

Again the equation for a_0 reduces to $a_0^5 = 0$

The equation for determining a_1 in this case however has no zero roots. It is obtained by equating to zero the coefficient of $\sin^4 \theta/_2$ in the numerator of $\frac{dy}{d\bar{\theta}}$ and is

$$\left[a_1(8c_{44}+\varepsilon\sin^2 2\phi) - 8\varepsilon\sin 2\phi\cos 2\phi\right]\left[c_{11}c_{44}(a_1^2+4) + \varepsilon(c_{11}+c_{12})\left\{\tfrac{1}{2}a_1^2\sin 2\phi + 2a_1\cos 2\phi - 2\sin 2\phi\right\}^2\right]$$

$$- \left[16c_{11} + 4c_{44}a_1^2 + 4\varepsilon\sin 2\phi\left(\tfrac{1}{2}a_1^2\sin 2\phi + 2a_1\cos 2\phi - 2\sin 2\phi\right)\right] \times \left[4c_{11}c_{44}\, a_1(a_1^4+4)\right.$$

$$\left. + 2\varepsilon(c_{11}+c_{12})(a_1\sin 2\phi + 2\cos 2\phi)\left\{\tfrac{1}{2}a_1^2\sin 2\phi + 2a_1\cos 2\phi - 2\sin 2\phi\right\}\right] = 0.$$

No attempt has been made to collect the terms in this equation, as the coefficients are awkward expressions. However, we consider the constant term, which is

$$-32\varepsilon\sin 2\phi\cos 2\phi\left[\varepsilon(c_{11}+c_{12}) + 4c_{11}(c_{11}+c_{12}-c_{44})\right].$$

This is only zero if $\varepsilon = 0$ or $\sin\phi = \cos\phi = \frac{1}{\sqrt{2}}$ (the case $\phi = 0$ to ~~lowest~~ zero order in $\theta/_2$ is included in case 1) i.e. we have anisotropy. Then, as is shown in the last section the position of the spot is given by an equation of the form

$$\bar{\theta} = C\cdot\sin^2\frac{\theta}{2}\cdot\bar{\phi}.$$

Thus, in general, for points on the axis the extra spots have an angular deflection from the Laue spot of an amount of the order of $\sin\frac{\theta}{2}\cdot\bar{\phi}$. The cases where the deflection is of the order of $\bar{\phi}\,\sin^2\frac{\theta}{2}$ are (i) complete isotropy, (ii) the indices of the Laue spot have either κ_1 or κ_3 zero,

(iii) κ_1 and κ_3 are equal. In those cases the results agree with experiment. However, we have no exact experimental observations for the case of $\kappa_1 \neq \kappa_3 \neq 0$, and would suggest that an examination be made of the regions surrounding such Laue spots.

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SUPPLEMENTARY PAPER.

RECIPROCITY VI. THE WAVE EQUATION OF THE MESON.

(Accepted for publication in the Proc.Roy.Soc.Edin.)

RECIPROCITY. Part VI.
THE WAVE FUNCTION OF THE MESON.

1. Introduction.

In this paper the equations of the meson are treated in the same manner as the Dirac Equation in a previous paper (K. Fuchs. IV)* [1] We use the formulae developed by Kemmer, [2] with a small modification, introduced so that the set of Maxwell's equations for the electro-magnetic field is obtained as a special case.

In the usual notation the 'classical' meson equations are

$$\frac{\partial \phi_\beta}{\partial x_\alpha} - \frac{\partial \phi_\alpha}{\partial x_\beta} = \varepsilon_1' \chi_{\alpha\beta},$$

$$\frac{\partial \chi_{\alpha\beta}}{\partial x_\alpha} = \varepsilon_2' \phi_\beta .$$

where the two constants are usually taken both equal to $\frac{m_0 c}{\hbar}$, and m_0 is the rest mass. (Some authors [3] put $\varepsilon_1' = 1$, $\varepsilon_2' = \left(\frac{m_0 c}{\hbar}\right)^2$ which is equivalent to the first definition, since only the product $\varepsilon_1' \varepsilon_2'$ matters). We prefer to keep the constants separate in order to be able to go to the limit $\varepsilon_1' = 0$ $\varepsilon_2' = 1$. This process leads to Maxwell's equations, which are in this way included in the following considerations.

2. The Angular Momentum Operator.

In (r, t) space the operator of the four-vector

* References to previous papers of this series are denoted by a Roman numeral, which preceeds the equation number.

of momentum and energy of the meson may be taken to be

(2.1) $$p_k = \frac{\hbar}{i} \frac{\partial}{\partial x^k}.$$

where

$$x_0, x_1, x_2, x_3 = ct, x, y, z.$$

$$x^k = g^{kl} x_l, \quad g^{kl} = \begin{cases} 0 & k \neq l \\ 1 & k = l \neq 0 \\ -1 & k = l = 0, \end{cases}$$

The angular momentum operator in four dimensions is defined in the usual way to be

(2.2) $$M^{kl} = x^k p^l - x^l p^k.$$

This is a six-vector, of which three components form the three-dimensional angular momentum vector $\underline{M}$ and the other three components another three vector $\underline{N}$.

(2.3) $$M_x = M^{23} \qquad M_y = M^{31} \qquad M_z = M^{12}.$$
$$N_x = M^{01} \qquad N_y = M^{02} \qquad N_z = N^{03}.$$

The commutation relations of these operators, and the results of operating on the angular dependent part of the solution of the Klein-Gordon equation with them, are given in (IV § 1.)

3. The wave equation of the meson.

In the case of the Klein-Gordon equation and the Dirac equation the angular dependent part of the wave operator was expressed in terms of the angular momentum. A similar treatment is possible here. The wave equation of the meson is taken in the form, (Kemmer, 1939)

$$\left(\hbar/i \; \beta^k \frac{\partial}{\partial x^k} - iP_\beta\right) \psi^P = 0,$$

i.e

(3.1) $$(\beta^k p_k - iP_\beta)\, \psi^P = 0.$$

The P is split out from the matrix β to bring the equations into the same form as the Dirac equation IV. This is of course not possible in the case of Maxwell's equations.

The β^k are matrices satisfying the commutation relations

$$\beta^k\beta^l\beta^m + \beta^m\beta^l\beta^k = g^{kl}\beta^m + g^{ml}\beta^k, \tag{3.2}$$

and β is a diagonal matrix chosen so that each component of ψ^P will satisfy the equation

$$(p_k p^k - P^2)\,\psi = 0, \tag{3.3}$$

which, for imaginary values of P, is the Klein-Gordon equation.

The wave equation (3·1) is slightly altered in form from the one proposed by Kemmer owing to a different choice of co-ordinates. We have taken as the fourth co-ordinate $x^0 = ct$, in place of $x^4 = ict$. Consequently, the relation between β^0 and β^4 is

$$\beta^0 = -i\beta^4.$$

Also β replaces the unit matrix.

As in previous papers of this series we transform to polar co-ordinates R, α, β, γ (in conformity with previous papers β is used to define one of the spherical co-ordinates, although it has already been used in the wave equation. However there is no danger of confusing the two meanings in what follows.). According to

$$\begin{cases} x^1 = R\cosh\alpha\sin\beta\cos\gamma, \\ x^2 = R\cosh\alpha\sin\beta\sin\gamma, \\ x^3 = R\cosh\alpha\cos\beta, \\ x^0 = R\sinh\alpha. \end{cases} \tag{3.4}$$

By use of the relations (IV 3·8, 3·9), we obtain the wave equation in terms of these co-ordinates,

$$(3.6)\qquad \left\{-\frac{1}{2R^2}\cdot\frac{i}{\hbar}\left[(x_k\beta^k),K^2\right]+\frac{\hbar}{i}\left(\frac{1}{R}\frac{\partial}{\partial R}+\frac{1}{2R^2}\right)(x_k p^k)-iP_\beta\right\}\psi^P=0,\qquad K^2=M^2-N^2.$$

The results, so far, hold for any set of β^k which satisfy (3·2) Kemmer has shown that there are three irreducible representations for the β^k . The representation which makes the wave equation correspond to Proca's equations will be used. Then the β^k may be written,

$$(3.6)\qquad \beta^k=\begin{pmatrix}0&0&0&\tilde{\gamma}_k\\0&0&\tilde{\alpha}_k&0\\0&\alpha_k&0&0\\\gamma_k&0&0&0\end{pmatrix};\quad k=1,2,3,\qquad \beta^0=\begin{pmatrix}0&0&-I&0\\0&0&0&0\\I&0&0&0\\0&0&0&0\end{pmatrix},$$

where

$$(3.7)\qquad \begin{matrix}\gamma_1=(-1,0,0)\\\gamma_2=(0,-1,0)\\\gamma_3=(0,0,-1)\end{matrix},\quad \alpha_1=\begin{pmatrix}0&0&0\\0&0&1\\0&-1&0\end{pmatrix},\quad \alpha_2=\begin{pmatrix}0&0&-1\\0&0&0\\1&0&0\end{pmatrix},\quad \alpha_3=\begin{pmatrix}0&1&0\\-1&0&0\\0&0&0\end{pmatrix},\quad I=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}.$$

and $\sim$ denotes the transposed of a matrix.

The most general form of β consistent with relativistic invariance is a ten row and column diagonal matrix, of which the first six diagonal elements are ε_1 , and the last four are ε_2 . ε_1 and ε_2 are connected by

$$\varepsilon_1\varepsilon_2=-1.$$

It is advantageous to take β in this form rather than the unit matrix, since, by a suitable choice of ε_1 and ε_2 , the wave equation leads immediately to Maxwell's equations for the electromagnetic field.

In order that the usual expressions appearing in the meson theory, which has been developed for imaginary P, (i.e. in terms of the rest mass) may still hold, the adjoint, ψ^+ of ψ, must satisfy, for imaginary values of P,

$$(3.9) \qquad P_k \psi^+ \beta^k + iP\psi^+\beta = 0,$$

$$\psi^+ = i\tilde{\psi}^* \eta_0, \quad \eta_0 = 2\beta_0\beta^0 - 1,$$

where $\tilde{\psi}^*$ is the transposed conjugate of ψ.

This condition arises from the necessity of the four-vector of charge and current (Kemmer, 1939. p 95)

$$\psi^+ \beta^k \psi$$

to satisfy the equation of continuity

$$(3.10) \qquad \frac{\partial}{\partial x^k}(\psi^+\beta^k\psi) = 0.$$

The validity of equation (3.10) requires that $\varepsilon_1 P$ and $\varepsilon_2 P$ shall be real, and therefore $\varepsilon_1, \varepsilon_2$ must be imaginary. Then of course the equation of continuity does not hold when P is real.

The commutation relations between β and the matrices β^k are

$$(3.11) \qquad [\beta, \beta^l\beta^k] = 0,$$

$$(3.12) \qquad \beta\beta^k + \beta^k\beta = (\varepsilon_1 + \varepsilon_2)\beta^k.$$

This last equation may be expressed in the more usual form

$$\beta\beta^k + \beta^k\beta = \beta^k.$$

by a different normalisation, but such a normalisation would not be convenient in this case.

4. The Spin Operators.

The four dimensional operator of total angular momentum is obtained by considering

$$(4.1) \qquad \int(x^i\theta^{k0} - x^k\theta^{i0})\,dV \quad \text{and} \quad \int(x^i\theta^{00} - x^0\theta^{i0})\,dV,$$

where θ^{ik} is the symmetrical tensor of energy and momentum. In our notation

$$(4.2a) \qquad \theta^{ik} = iP.c.\left\{ \psi^{+}(\beta^{i}\beta^{k}+\beta^{k}\beta^{i})\beta\psi - g^{ik}\psi^{+}\beta\psi \right\}$$

$$(4.2b) \qquad = \frac{c}{2}\left\{ \psi^{+}\beta^{i}p^{k}\psi - (p^{k}\psi^{+})\beta^{i}\psi \right\} - \frac{c\hbar}{2i}\frac{d}{dx^{\rho}}\left\{ \psi^{+}(\beta^{\rho}\beta^{k}\beta^{i} - \beta^{i}\beta^{k}\beta^{\rho})\psi \right\}.$$

Using the second form for θ^{ik} and the commutation relations for β^{k} gives

$$(4.3) \qquad \begin{cases} P^{ik} = \int (x^{i}\theta^{k0} - x^{k}\theta^{i0})\, dV \\ \quad = c\int \left\{ \psi^{+}\beta^{0}(x^{i}p^{k} - x^{k}p^{i})\psi + \frac{\hbar}{i}\psi^{+}(\beta^{i}\beta^{k} - \beta^{k}\beta^{i})\beta^{0}\psi \right\} dV. \\ P^{0k} = \int (x^{0}\theta^{k0} - x^{k}\theta^{00})\, dV. \\ \quad = c\int \left\{ \psi^{+}\beta^{0}(x^{0}p^{k} - x^{k}p^{0})\psi + \frac{\hbar}{i}\psi^{+}\left(\beta^{0}\frac{\beta^{0}\beta^{k}+\beta^{k}\beta^{0}}{2} + \frac{\beta^{0}\beta^{k}+\beta^{k}\beta^{0}}{2}\beta^{0}\right)\psi \right\} dV. \end{cases}$$

According to Kemmer, (1939. p. 96.), the expectation value of an observable with operator ω is $\int \psi^{+}\,\overline{\overline{\beta^{0}\omega}}\,\psi\, dV$ where $\overline{\overline{\beta^{0}\omega}}$ denotes $\beta^{0}\omega$ when β^{0} and ω commute, but a symmetrical combination of them when they do not. Taking this symmetrical combination to be $\frac{\beta^{0}\omega + \omega\beta^{0}}{2}$ and observing that $(\beta^{i}\beta^{k} - \beta^{k}\beta^{i})$ (when $i, k = 1, 2, 3$) commutes with β^{0} we see the total angular momentum operator in four dimensions is

$$(4.4) \qquad {}^{s}M^{kl} = (x^{k}p^{l} - x^{l}p^{k}) + \frac{\hbar}{i}(\beta^{k}\beta^{l} - \beta^{l}\beta^{k}),$$

and the spin operator is

$$(4.5) \qquad S^{kl} = \frac{\beta^{k}\beta^{l} - \beta^{l}\beta^{k}}{i}.$$

In the usual way the three-vectors ${}^{S}\underline{M}$, ${}^{S}\underline{N}$ and also $\underline{S}^{M}$, $\underline{S}^{N}$ are introduced.

$$
(4.6)\quad
\begin{aligned}
&{}^{S}M^{23} = {}^{S}M_x = M_x + \hbar S_x^M, \quad {}^{S}M^{31} = {}^{S}M_y = M_y + \hbar S_y^M, \quad {}^{S}M^{12} = {}^{S}M_z = M_z + \hbar S_z^M. \\
&{}^{S}M^{01} = {}^{S}N_x = N_x + \hbar S_x^N, \quad {}^{S}M^{02} = {}^{S}N_y = N_y + \hbar S_y^N, \quad {}^{S}M^{03} = {}^{S}N_z = N_z + \hbar S_z^N.
\end{aligned}
$$

The squares of the operators ${}^{S}\underline{M}$, ${}^{S}\underline{N}$ are

$$
(4.7)\quad
\begin{aligned}
{}^{S}M^2 &= M^2 + 2\hbar(\underline{M}.\underline{S}^M) + \hbar^2 S^{M^2}. \\
{}^{S}N^2 &= N^2 + 2\hbar(\underline{N}.\underline{S}^N) + \hbar^2 S^{N^2}.
\end{aligned}
$$

The commutation relations for the spin operators are similar to those appearing in the case of Dirac's equation, i.e. in our case they are:-

$$
(4.8)\quad
\begin{aligned}
\left[S_x^M, S_y^M\right] &= \left[S_x^N, S_y^N\right] = i S_z^M. \\
\left[S_x^M, S_y^N\right] &= \left[S_x^N, S_y^M\right] = i S_z^N.
\end{aligned}
$$

Also the operators ${}^{S}M_z$, ${}^{S}M^2$, ${}^{S}N^2$ commute with each other

$$
(4.9)\quad \left[{}^{S}M_z, {}^{S}M^2\right] = \left[{}^{S}M_z, {}^{S}N^2\right] = \left[{}^{S}M^2, {}^{S}N^2\right] = 0.
$$

The invariant

$$
{}^{S}K^2 = {}^{S}M^2 - {}^{S}N^2.
$$

is introduced, and obviously commutes with ${}^{S}M_z$ and ${}^{S}M^2$.

The operators ${}^{S}M_z$, ${}^{S}M^2$, ${}^{S}K^2$, also commute with the wave operator.

5. <u>The Representation of the Spin Operator</u>.

5. The Representation of the Spin Operator.

Using the representation for the β^k given in (3·6, 3·7), the spin matrices may be written in the form

$$(5.1)\qquad S_x^M = \frac{1}{i}\begin{pmatrix}\alpha_1 & 0 & 0 & 0\\ 0 & \alpha_1 & 0 & 0\\ 0 & 0 & \alpha_1 & 0\\ 0 & 0 & 0 & 0\end{pmatrix};\quad S_y^M = \frac{1}{i}\begin{pmatrix}\alpha_2 & 0 & 0 & 0\\ 0 & \alpha_2 & 0 & 0\\ 0 & 0 & \alpha_2 & 0\\ 0 & 0 & 0 & 0\end{pmatrix};\quad S_z^M = \frac{1}{i}\begin{pmatrix}\alpha_3 & 0 & 0 & 0\\ 0 & \alpha_3 & 0 & 0\\ 0 & 0 & \alpha_3 & 0\\ 0 & 0 & 0 & 0\end{pmatrix}.$$

$$(5.2)\qquad S_x^N = \frac{1}{i}\begin{pmatrix}0 & \tilde{\alpha}_1 & 0 & 0\\ \alpha_1 & 0 & 0 & 0\\ 0 & 0 & 0 & \tilde{\gamma}_1\\ 0 & 0 & \gamma_1 & 0\end{pmatrix};\quad S_y^N = \frac{1}{i}\begin{pmatrix}0 & \tilde{\alpha}_2 & 0 & 0\\ \alpha_2 & 0 & 0 & 0\\ 0 & 0 & 0 & \tilde{\gamma}_2\\ 0 & 0 & \gamma_2 & 0\end{pmatrix};\quad S_z^N = \frac{1}{i}\begin{pmatrix}0 & \tilde{\alpha}_3 & 0 & 0\\ \alpha_3 & 0 & 0 & 0\\ 0 & 0 & 0 & \tilde{\gamma}_3\\ 0 & 0 & \gamma_3 & 0\end{pmatrix}.$$

where α and γ are defined in (3·8)

All the matrices in (5·1) and (5·2) are square, with ten rows and columns.

Then in the expressions (4·9) for the squares of $S\underline{M}$, and $S\underline{N}$, we shall have

$$(5.3)\qquad (\underline{S}^M.\underline{M}) = \frac{1}{i}\begin{pmatrix}(\alpha.M) & 0 & 0 & 0\\ 0 & (\alpha.M) & 0 & 0\\ 0 & 0 & (\alpha.M) & 0\\ 0 & 0 & 0 & 0\end{pmatrix};\qquad (5.4)\qquad S^{M^2} = 2\begin{pmatrix}I & 0 & 0 & 0\\ 0 & I & 0 & 0\\ 0 & 0 & I & 0\\ 0 & 0 & 0 & 0\end{pmatrix}.$$

$$(5.5)\qquad (\underline{S}^N.\underline{N}) = \frac{1}{i}\begin{pmatrix}0 & (\tilde{\alpha}.N). & 0 & 0\\ (\alpha N) & 0 & 0 & 0\\ 0 & 0 & 0 & (\tilde{\gamma}N)\\ 0 & 0 & (\gamma N) & 0\end{pmatrix};\qquad (5.6)\qquad S^{M^2} = \begin{pmatrix}2I & 0 & 0 & 0\\ 0 & 2I & 0 & 0\\ 0 & 0 & I & 0\\ 0 & 0 & 0 & 3\end{pmatrix}.$$

where we have written

$$(5.7)\qquad (\alpha.M) = \alpha_1 M_x + \alpha_2 M_y + \alpha_3 M_z = \begin{pmatrix}0 & M_z & -M_y\\ -M_z & 0 & M_x\\ M_y & -M_x & 0\end{pmatrix};\quad (\alpha.N) = (\alpha_1 N_x + \alpha_2 N_y + \alpha_3 N_z) = -(\tilde{\alpha}.N).$$

$$(\gamma.N) = \gamma_1 N_x + \gamma_2 N_y + \gamma_3 N_z = -(N_x, N_y, N_z);\quad (\tilde{\gamma}.N) = (\widetilde{\gamma.N}).$$

and I is the unit matrix with three rows and columns.

6. Proper Values of $^{s}M_z$, $^{s}M^2$ and $^{s}K^2$.

Since $^{s}M_z$, $^{s}M^2$, $^{s}K^2$ commute with each other they will have simultaneous proper functions. By observing the forms of the matrices representing these operators, we see that the proper value equation in each case will split up into four equations. Consequently we write the simultaneous proper function as

$$\Lambda = \begin{pmatrix} \chi^1 \\ \chi^2 \\ \chi^3 \\ \chi^0 \end{pmatrix}, \tag{6.1}$$

where χ^p, $p=1,2,3$ is a column matrix with three elements.

$$\chi^p = \begin{pmatrix} \chi^{p1} \\ \chi^{p2} \\ \chi^{p3} \end{pmatrix}, \tag{6.2}$$

and χ^0 is a column matrix with one element, i.e. a scalar quantity.

Let the simultaneous proper values of the operators $^{s}M_z$, $^{s}M^2$, $^{s}K^2$ be $\hbar\mu$, $\hbar^2\lambda(\lambda+1)$, $\hbar^2\nu$. Then using (5·1) – (5·6) the equations giving χ^p and χ^0 are,

$$(6.3)\quad \begin{cases} \text{(a)} & M_z\chi^p + \frac{\hbar}{i}\alpha_3\chi^p = \hbar\mu\chi^p. \\ \text{(b)} & M_z\chi^0 = \hbar\mu\chi^0. \end{cases}$$

$$(6.4)\quad \begin{cases} \text{(a)} & M^2\chi^p + \frac{2\hbar}{i}(\alpha . M)\chi^p + 2\hbar^2\chi^p = \hbar^2\lambda(\lambda+1)\chi^p. \\ \text{(b)} & M^2\chi^0 = \hbar^2\lambda(\lambda+1)\chi^0. \end{cases}$$

$$(6.5)\quad \begin{cases} \text{(a)} & (N^2 - 2\hbar^2 - \lambda(\lambda+1)\hbar^2 + \hbar^2\nu)\chi^1 + \frac{2\hbar}{i}(\tilde{\alpha}.N)\chi^2 = 0. \\ \text{(b)} & (N^2 - 2\hbar^2 - \lambda(\lambda+1)\hbar^2 + \hbar^2\nu)\chi^2 + \frac{2\hbar}{i}(\alpha.N)\chi^1 = 0. \\ \text{(c)} & (N^2 - \hbar^2 - \lambda(\lambda+1)\hbar^2 + \hbar^2\nu)\chi^3 + \frac{2\hbar}{i}(\tilde{\gamma}.N)\chi^0 = 0. \\ \text{(d)} & (N^2 - 3\hbar^2 - \lambda(\lambda+1)\hbar^2 + \hbar^2\nu)\chi^0 + \frac{2\hbar}{i}(\gamma.N)\chi^3 = 0. \end{cases}$$

Let ξ^p be a proper function of the operator ${}^sM_z$. Now ${}^sM_z$ commutes with M_z, M^2 and K^2, so these four operators can be brought simultaneously into diagonal form. Thus ξ^p will involve only one simultaneous proper function $f_{k,l,m}$ of M_z, M^2, K^2.

$$(6.6) \qquad \xi^p = \begin{pmatrix} a^{p1} f_{k,l,m} \\ a^{p2} f_{k,l,m} \\ a^{p3} f_{k,l,m} \end{pmatrix}; \qquad p = 1,2,3. \qquad \xi^0 = a^0 f_{k,l,m}.$$

Thus we have from (6·3a) and (6·3b) respectively,

$$(6.7) \qquad \begin{cases} \left(\hbar m a^{p1} + \frac{\hbar}{i} a^{p2}\right) f_{k,l,m} = \hbar\mu a^{p1} f_{k,l,m}. \\ \left(\hbar m a^{p2} - \frac{\hbar}{i} a^{p1}\right) f_{k,l,m} = \hbar\mu a^{p2} f_{k,l,m}. \\ \hbar m a^{p3} f_{k,l,m} = \hbar\mu a^{p3} f_{k,l,m}. \end{cases}$$

and
$$\hbar m a^0 f_{k,l,m} = \hbar\mu a^0 f_{k,l,m}.$$

Equating to zero the coefficients of $f_{k,l,m}$ in these equations, gives four linear equations for $a^{p1}, a^{p2}, a^{p3}, a^0$. The secular equation for these has three solutions.

$$(6.8) \qquad m = \mu+1, \ \mu, \ \mu-1.$$

Correspondingly we obtain three independent expressions for the three columns

$$(6.9) \qquad \xi^{p+} = \begin{pmatrix} i\, f_{k,l,\mu+1} \\ f_{k,l,\mu+1} \\ 0 \end{pmatrix}; \qquad \xi^{p0} = \begin{pmatrix} 0 \\ 0 \\ f_{k,l,\mu} \end{pmatrix}; \qquad \xi^{p-} = \begin{pmatrix} -i f_{k,l,\mu-1} \\ f_{k,l,\mu-1} \\ 0 \end{pmatrix}.$$

and for ξ^0

$$(6.10) \qquad \xi^{0+} = 0; \qquad \xi^{00} = f_{k,l,\mu}; \qquad \xi^{0-} = 0.$$

Equation (6·4a) reduces to

$$(M^2 - \lambda(\lambda+1)\hbar^2 + 2\hbar^2)\chi^{P1} + \frac{2\hbar}{i}\left(M_z\chi^{P2} - M_y\chi^{P3}\right) = 0.$$

$$(6{\cdot}11) \qquad (M^2 - \lambda(\lambda+1)\hbar^2 + 2\hbar^2)\chi^{P2} + \frac{2\hbar}{i}\left(M_x\chi^{P3} - M_z\chi^{P1}\right) = 0.$$

$$(M^2 - \lambda(\lambda+1)\hbar^2 + 2\hbar^2)\chi^{P3} + \frac{2\hbar}{i}\left(M_y\chi^{P1} - M_x\chi^{P2}\right) = 0.$$

Since ${}^sM^2$ commutes with M^2 and K^2 as well as with ${}^sM_z$ we can assume the simultaneous proper functions of ${}^sM^2$ and ${}^sM'_z$ as linear combinations of the three proper functions (6·9) of ${}^sM_z$, ie

$$(6{\cdot}12) \qquad \begin{pmatrix} i c_1 f_{k,l,\mu-1} + i c_2 f_{k,l,\mu+1} \\ -c_1 f_{k,l,\mu-1} + c_2 f_{k,l,\mu+1} \\ B f_{k,l,\mu} \end{pmatrix}.$$

By using the relations (IV, 2·8) we obtain, after reduction,

$$c_1\left(i\gamma - \frac{2}{i}(\mu-1)\right) + B(l-\mu+1) = 0.$$

$$(6{\cdot}13) \qquad c_2\left(i\gamma + \frac{2}{i}(\mu+1)\right) - B(l+\mu+1) = 0.$$

$$B\gamma + 2ic_1(l+\mu) - 2ic_2(l-\mu) = 0.$$

$$\gamma = l(l+1) + 2 - \lambda(\lambda+1).$$

When we make the secular determinant vanish, we obtain,

$$(6{\cdot}14) \qquad l = \lambda-1, \quad \lambda, \quad \lambda+1.$$

and (6·13) gives the corresponding ratios of

The three independent solutions are

$$(6{\cdot}15) \qquad \Omega^-_{k,\lambda,\mu} = \begin{pmatrix} f_{k,\lambda-1,\mu-1} - f_{k,\lambda-1,\mu+1} \\ i(f_{k,\lambda-1,\mu-1} + f_{k,\lambda-1,\mu+1}) \\ 2 f_{k,\lambda-1,\mu} \end{pmatrix}; \quad \Omega^0_{k,\lambda,\mu} = \begin{pmatrix} (\lambda-\mu+1) f_{k,\lambda,\mu-1} + (\lambda+\mu+1) f_{k,\lambda,\mu+1} \\ i\left((\lambda-\mu+1) f_{k,\lambda,\mu-1} - (\lambda+\mu+1) f_{k,\lambda,\mu+1}\right) \\ -2\mu f_{k,\lambda,\mu} \end{pmatrix}$$

$$\Omega^+_{k,\lambda,\mu} = \begin{pmatrix} (\lambda-\mu+1)(\lambda-\mu+2) f_{k,\lambda+1,\mu-1} - (\lambda+\mu+1)(\lambda+\mu+2) f_{k,\lambda+1,\mu+1} \\ i\left((\lambda-\mu+1)(\lambda-\mu+2) f_{k,\lambda+1,\mu-1} + (\lambda+\mu+1)(\lambda+\mu+2) f_{k,\lambda+1,\mu+1}\right) \\ -2(\lambda-\mu+1)(\lambda+\mu+1) f_{k,\lambda+1,\mu} \end{pmatrix}.$$

The solution of (6·4b) which also satisfies (6·3b) is $f_{\kappa,\lambda,\mu}$. Finally we consider equations (6·5). Using the expression (5·7) for (α, N) and $(\tilde{\alpha}. N)$ (6·5a) may be written

$$(6\cdot16)\qquad \begin{aligned} &\left(N^2 - 2\hbar^2 - \lambda(\lambda+1)\hbar^2 + \hbar^2\nu\right)\chi^{11} - \frac{2\hbar}{i}\left(N_z\chi^{22} - N_y\chi^{23}\right) = 0. \\ &\left(N^2 - 2\hbar^2 - \lambda(\lambda+1)\hbar^2 + \hbar^2\nu\right)\chi^{12} - \frac{2\hbar}{i}\left(N_x\chi^{23} - N_z\chi^{21}\right) = 0. \\ &\left(N^2 - 2\hbar^2 - \lambda(\lambda+1)\hbar^2 + \hbar^2\nu\right)\chi^{13} - \frac{2\hbar}{i}\left(N_y\chi^{21} - N_x\chi^{22}\right) = 0. \end{aligned}$$

(6·5b) gives three similar equations with χ^1 replaced by χ^2 and χ^2 by $-\chi^1$.

(6·5c) and (6·5d) may be written

$$(6\cdot17)\qquad \left(N^2 - \hbar^2 - \lambda(\lambda+1)\hbar^2 + \hbar^2\nu\right)\begin{pmatrix}\chi^{31}\\ \chi^{32}\\ \chi^{33}\end{pmatrix} - \frac{2\hbar}{i}\begin{pmatrix}N_x\\ N_y\\ N_z\end{pmatrix}\chi^0 = 0.$$

$$(6\cdot18)\qquad \left(N^2 - 3\hbar^2 - \lambda(\lambda+1)\hbar^2 + \hbar^2\nu\right)\chi^0 - \frac{2\hbar}{i}\left(N_x\chi^{31} + N_y\chi^{32} + N_z\chi^{33}\right) = 0.$$

Since ${}^sK^2$ commutes with K^2 each of the three columns χ^2 of the simultaneous proper functions of ${}^sM_z$ ${}^sM^2$, ${}^sK^2$ can be taken as a linear combination of the functions (6·15).

Thus the proper functions will be of the form

$$(6\cdot19)\qquad \begin{aligned} \chi^p &= A^{p-}\Omega^-_{\kappa,\lambda,\mu} + A^{p0}\Omega^0_{\kappa,\lambda,\mu} + A^{p+}\Omega^+_{\kappa,\lambda,\mu}. \\ \chi^0 &= A^{00} f_{\kappa,\lambda,\mu}. \end{aligned}$$

By use of relations (IV, 2·15), (6·16) gives, after reduction,

$$(6\cdot20)\qquad \begin{aligned} &(\gamma-2\lambda)A^{1-} + 2i\,A^{20}\,\frac{\lambda^2(\lambda+1)}{2\lambda+1} = 0 \\ &A^{10}\gamma - 2i\,A^{2-}\,\frac{(\lambda-\kappa-1)(\lambda+\kappa+1)}{\lambda^2} + 2i\,A^{2+}(\lambda+1)^2 = 0 \\ &A^{1+}(\gamma+2\lambda+2) - 2i\,A^{20}\,\frac{\lambda(\lambda-\kappa)(\lambda+\kappa+2)}{(2\lambda+1)(\lambda+1)^2} = 0 \end{aligned}$$

and (6·17) and (6·18) lead to

$$A^{30} = 0 ,$$

(6·21)
$$(\gamma - 2\lambda - 1) A^{3-} + \frac{\lambda^2}{2\lambda+1} A^{00} = 0 ,$$

$$(\gamma + 2\lambda + 1) A^{3+} + \frac{(\lambda - k)(\lambda + k + 2)}{(2\lambda+1)(\lambda+1)^2} A^{00} = 0 ,$$

$$(\gamma - 3) A^{00} - 4 \frac{(\lambda - k - 1)(\lambda + k + 1)}{\lambda} A^{3-} - 4(\lambda+1)^3 A^{3+} = 0 ,$$

where

$$\gamma = -[k(k+2) - \nu + 2] .$$

There is also a set of equations similar to (6·20) with A^{1-}, A^{10}, A^{1+} replaced by A^{2-}, A^{20}, A^{2+}, and A^{2-}, A^{20}, A^{2+} replaced by $-A^{1-}, -A^{10}, -A^{1+}$. The vanishing of the secular determinant gives six values for k by

(6·22) $\nu = (k-1)(k+1)$; $\nu = k^2$; $\nu = k(k+2)$; $\nu = (k+1)^2$; $\nu = (k+1)(k+3)$; $\nu = (k+2)^2$.

We have thus obtained two independent sets of simultaneous proper functions of ${}^sM_z$, ${}^sM^2$ and ${}^sK^2$. One set has the proper value of ${}^sK^2$ in the form $\hbar^2 k(k+2)$ and the other has it in the form $\hbar^2 (k+1)^2$ where in each case k is a positive integer.

The proper functions are

(A) Those having proper values $\hbar\mu$, $\hbar^2\lambda(\lambda+1)$, $\hbar^2(k+1)^2$

$$(6.23)\quad \begin{cases} {}^{a}\chi^{1\pm}_{\kappa,\lambda,\mu} = \frac{\lambda}{2\lambda+1}\Omega^{-}_{\kappa\pm1,\lambda,\mu} + \frac{(\lambda+1\pm(\kappa+1))(\lambda+2\pm(\kappa+1))}{(2\lambda+1)(\lambda+1)^{3}}\Omega^{+}_{\kappa\pm1,\lambda,\mu} \\ {}^{a}\chi^{2\pm}_{\kappa,\lambda,\mu} = -i\,\frac{\lambda+1\pm(\kappa+1)}{\lambda(\lambda+1)}\Omega^{0}_{\kappa\pm1,\lambda,\mu} \\ {}^{a}\chi^{3\pm}_{\kappa,\lambda,\mu} = 0 \\ {}^{a}\chi^{0\pm}_{\kappa,\lambda,\mu} = 0 \end{cases} \quad \begin{cases} {}^{b}\chi^{1\pm}_{\kappa,\lambda,\mu} = -{}^{a}\chi^{2\pm}_{\kappa,\lambda,\mu} \\ {}^{b}\chi^{2\pm}_{\kappa,\lambda,\mu} = {}^{a}\chi^{1\pm}_{\kappa,\lambda,\mu} \\ {}^{b}\chi^{3\pm}_{\kappa,\lambda,\mu} = 0 \\ {}^{b}\chi^{0\pm}_{\kappa,\lambda,\mu} = 0 \end{cases} \quad \begin{cases} {}^{c}\chi^{10}_{\kappa,\lambda,\mu} = 0 \\ {}^{c}\chi^{20}_{\kappa,\lambda,\mu} = 0 \\ {}^{c}\chi^{30}_{\kappa,\lambda,\mu} = \frac{\lambda}{2\lambda+1}\Omega^{-}_{\kappa,\lambda,\mu} - \frac{(\lambda-\kappa)(\lambda+\kappa+2)}{(2\lambda+1)(\lambda+1)}\Omega^{+}_{\kappa,\lambda,\mu} \\ {}^{c}\chi^{00}_{\kappa,\lambda,\mu} = 2f_{\kappa,\lambda,\mu}. \end{cases}$$

(B) Those having proper values $\hbar\mu$, $\hbar^2\lambda(\lambda+1)$, $\hbar^2\kappa(\kappa+2)$

$$(6.24)\quad \begin{cases} {}^{a}\chi^{10}_{\kappa,\lambda,\mu} = \frac{i\lambda^2}{2\lambda+1}\Omega^{-}_{\kappa,\lambda,\mu} + \frac{i(\lambda\mp\kappa)(\lambda+\kappa+2)}{(2\lambda+1)(\lambda+1)^2}\Omega^{+}_{\kappa,\lambda,\mu} \\ {}^{a}\chi^{20}_{\kappa,\lambda,\mu} = \Omega^{0}_{\kappa,\lambda,\mu} \\ {}^{a}\chi^{30}_{\kappa,\lambda,\mu} = 0 \\ {}^{a}\chi^{00}_{\kappa,\lambda,\mu} = 0 \end{cases} \quad \begin{cases} {}^{b}\chi^{10}_{\kappa,\lambda,\mu} = -{}^{a}\chi^{20}_{\kappa,\lambda,\mu} \\ {}^{b}\chi^{20}_{\kappa,\lambda,\mu} = {}^{a}\chi^{10}_{\kappa,\lambda,\mu} \\ {}^{b}\chi^{30}_{\kappa,\lambda,\mu} = 0 \\ {}^{b}\chi^{00}_{\kappa,\lambda,\mu} = 0 \end{cases} \quad \begin{aligned} &{}^{c}\chi^{1\pm}_{\kappa,\lambda,\mu} = 0 \\ &{}^{c}\chi^{2\pm}_{\kappa,\lambda,\mu} = 0 \\ &{}^{c}\chi^{3\pm}_{\kappa,\lambda,\mu} = \frac{\lambda^2}{2(2\lambda+1)}\Omega^{-}_{\kappa\pm1,\lambda,\mu} - \frac{(\lambda+1\pm\overline{\kappa+1})(\lambda+2\pm\overline{\kappa+1})}{2(2\lambda+1)(\lambda+1)^2}\Omega^{+}_{\kappa\pm1,\lambda,\mu} \\ &{}^{c}\chi^{0\pm}_{\kappa,\lambda,\mu} = -(\lambda+1\pm\overline{\kappa+1})f_{\kappa\pm1,\lambda,\mu}. \end{aligned}$$

The Solution of the Wave Equation.

The wave equation has already been expressed in terms of polar co-ordinates in (3·5)

$$(7.1)\quad \left\{\frac{1}{2R^2}\frac{i}{\hbar}\left[(x_\mu\beta^\mu), K^2\right] + \frac{\hbar}{i}\left(\frac{1}{R}\frac{\partial}{\partial R} + \frac{1}{2R^2}\right)(x_\mu\beta^\mu) - iP_\beta\right\}\psi = 0.$$

It is easily shown that the wave operator commutes with the operators ${}^{s}M_z$, ${}^{s}M^2$, ${}^{s}K^2$. Consequently the solutions of the wave equation are linear combinations of the proper solutions given in

(6·23) and (6·24). The coefficients in these linear combinations must be functions of R.

We consider the quantity $(x_\mu \beta^\mu)$ which appears in the wave operator. If we write

$$\psi = \begin{pmatrix} \psi^1 \\ \psi^2 \\ \psi^3 \\ \psi^0 \end{pmatrix}, \tag{7.2}$$

where ψ^p, $p = 1,2,3$ is a column vector with three components, and ψ^0 a column with one element

$$(x_\mu \beta^\mu)\,\psi = \begin{pmatrix} -x_0\,\psi^3 + (x.\tilde{\gamma})\,\psi^0 \\ -(x.\alpha)\,\psi^3 \\ x_0\,\psi^1 + (x.\alpha)\,\psi^2 \\ -(x_1, x_2, x_3)\,\psi^1 \end{pmatrix}, \tag{7.3}$$

where

$$(x.\alpha) = x_1\alpha_1 + x_2\alpha_2 + x_3\alpha_3\,; \quad (x\,\tilde{\gamma}) = x_1\tilde{\gamma}_1 + x_2\tilde{\gamma}_2 + x_3\tilde{\gamma}_3\,.$$

We consider the results of operating with on the simultaneous proper functions (6.23)

Using relations (IV, 2·24, 2·25) and remembering $x_0 = -x^0$ we have

$$\left\{\begin{aligned} -x_0\;{}^c\chi^{30}_{\kappa,\lambda,\mu} + (x\tilde{\gamma})\;{}^c\chi^{00}_{\kappa,\lambda,\mu} &= -\frac{iR}{2}\left({}^a\chi^{1+}_{\kappa,\lambda,\mu} + {}^a\chi^{1-}_{\kappa,\lambda,\mu}\right). \\ -(x.\alpha)\;{}^c\chi^{30}_{\kappa,\lambda,\mu} &= -\frac{iR}{2}\left({}^a\chi^{2+}_{\kappa,\lambda,\mu} + {}^a\chi^{2-}_{\kappa,\lambda,\mu}\right). \\ x_0\;{}^a\chi^{1\pm}_{\kappa,\lambda,\mu} + (x.\alpha)\;{}^a\chi^{2\pm}_{\kappa,\lambda,\mu} &= iR\;{}^c\chi^{30}_{\kappa,\lambda,\mu}. \\ -(x_1,x_2,x_3)\;{}^a\chi^{1\pm}_{\kappa,\lambda,\mu} &= iR.\;{}^c\chi^{00}_{\kappa,\lambda,\mu}. \end{aligned}\right. \tag{7.4}$$

and

$$\left\{\begin{aligned} x_0\;{}^b\chi^{1\pm}_{\kappa,\lambda,\mu} + (x_1\alpha)\;{}^b\chi^{2\pm}_{\kappa,\lambda,\mu} &= 0. \\ -(x_1,x_2,x_3)\;{}^b\chi^{1\pm}_{\kappa,\lambda,\mu} &= 0. \end{aligned}\right.$$

Each component of the wave function satisfies the Klein-Gordon equation (3·3). Thus, from a consideration of the relations (7·4), we see that $^{b}\chi^{1\pm}$ and $^{b}\chi^{2\pm}$ will not appear in the wave function, which is, consequently, of the form

$$(7.5)\qquad \begin{pmatrix} A^{+}\,\frac{1}{R} Z_{\kappa+2}\ {}^{a}\chi^{1+}_{\kappa,\lambda,\mu} + A^{-}\,\frac{1}{R} Z_{\kappa}\ {}^{a}\chi^{1-}_{\kappa,\lambda,\mu} \\ A^{+}\,\frac{1}{R} Z_{\kappa+2}\ {}^{a}\chi^{2+}_{\kappa,\lambda,\mu} + A^{-}\,\frac{1}{R} Z_{\kappa}\ {}^{a}\chi^{2-}_{\kappa,\lambda,\mu} \\ 2A^{0}\ \frac{1}{R}\, Z_{\kappa+1}\ {}^{c}\chi^{30}_{\kappa,\lambda,\mu} \\ 2A^{0}\ \frac{1}{R}\, Z_{\kappa+1}\ {}^{c}\chi^{00}_{\kappa,\lambda,\mu} \end{pmatrix},$$

where the argument of the Bessel Function Z is $PR/\hbar$.

When we substitute in the wave equation, and use the recurrence formulae for the Bessel function,

$$(7.6)\qquad \begin{aligned} \left(\frac{d}{dR} + \frac{1}{2R}\right) Z_n\left(\frac{PR}{\hbar}\right) &= -\frac{n-\frac{1}{2}}{R}\, Z_n\left(\frac{PR}{\hbar}\right) + \frac{P}{\hbar}\, Z_{n-1}\left(\frac{PR}{\hbar}\right) \\ &= \frac{n+\frac{1}{2}}{R}\, Z_n\left(\frac{PR}{\hbar}\right) - \frac{P}{\hbar}\, Z_{n+1}\left(\frac{PR}{\hbar}\right), \end{aligned}$$

we get for the constants

$$A^{-} = -A^{+}, \qquad A^{0} = i\varepsilon_1 A^{+}.$$

Thus a solution of the wave equation is

$$(7.7)\qquad \begin{pmatrix} \frac{1}{R} Z_{\kappa+2}\left(\frac{PR}{\hbar}\right) {}^{a}\chi^{1+}_{\kappa,\lambda,\mu} - \frac{1}{R} Z_{\kappa}\left(\frac{PR}{\hbar}\right) {}^{a}\chi^{1-}_{\kappa,\lambda,\mu} \\ \frac{1}{R} Z_{\kappa+2}\left(\frac{PR}{\hbar}\right) {}^{a}\chi^{2+}_{\kappa,\lambda,\mu} - \frac{1}{R} Z_{\kappa}\left(\frac{PR}{\hbar}\right) {}^{a}\chi^{2-}_{\kappa,\lambda,\mu} \\ \frac{2i\varepsilon_1}{R}\, Z_{\kappa+1}\left(\frac{PR}{\hbar}\right) {}^{c}\chi^{30}_{\kappa,\lambda,\mu} \\ \frac{2i\varepsilon_1}{R}\, Z_{\kappa+1}\left(\frac{PR}{\hbar}\right) {}^{c}\chi^{00}_{\kappa,\lambda,\mu} \end{pmatrix} = {}^{1}\psi^{P}_{\kappa,\lambda,\mu}(R,\alpha,\beta,\gamma).$$

We can find another independent solution of the wave equation involving the proper functions with proper value $\hbar^2 \kappa(\kappa+2)$ for S_K^2.

With the notation of (6·24)

$$(7.8)\quad \begin{cases} -x_0 \; {}^c\chi^{3\pm}_{\kappa,\lambda,\mu} + (x,\tilde{\gamma}) \; {}^c\chi^{0\pm}_{\kappa,\lambda,\mu} = -\frac{R}{2} \; {}^a\chi^{10}_{\kappa,\lambda,\mu}. \\ \qquad -(x,\alpha) \; {}^c\chi^{3\pm}_{\kappa,\lambda,\mu} = -\frac{R}{2} \; {}^a\chi^{20}_{\kappa,\lambda,\mu}. \\ x_0 \; {}^a\chi^{10}_{\kappa,\lambda,\mu} + (x,\alpha) \; {}^a\chi^{20}_{\kappa,\lambda,\mu} = -R\left(\frac{\kappa+2}{\kappa+1} \; {}^c\chi^{3-}_{\kappa,\lambda,\mu} + \frac{\kappa}{\kappa+1} \; {}^c\chi^{3+}_{\kappa,\lambda,\mu}\right). \\ \qquad -(x_1,x_2,x_3) \; {}^a\chi^{10}_{\kappa,\lambda,\mu} = -R\left(\frac{\kappa+2}{\kappa+1} \; {}^c\chi^{0-}_{\kappa,\lambda,\mu} + \frac{\kappa}{\kappa+1} \; {}^c\chi^{0+}_{\kappa,\lambda,\mu}\right). \end{cases}$$

and

$$\begin{cases} x_0 \; {}^b\chi^{10}_{\kappa,\lambda,\mu} + (x,\alpha) \; {}^b\chi^{20}_{\kappa,\lambda,\mu} = 0. \\ \qquad -(x_1,x_2,x_3) \; {}^b\chi^{10}_{\kappa,\lambda,\mu} = 0. \end{cases}$$

In this case the corresponding solution of the wave equation is

$$(7.9)\quad \begin{pmatrix} \frac{1}{R} \, Z_{\kappa+1}\left(\frac{PR}{\hbar}\right) \; {}^a\chi^{10}_{\kappa,\lambda,\mu} \\ \frac{1}{R} \, Z_{\kappa+1}\left(\frac{PR}{\hbar}\right) \; {}^a\chi^{20}_{\kappa,\lambda,\mu} \\ \frac{\varepsilon_1}{R}\left(\frac{\kappa}{\kappa+1} Z_{\kappa+2}\left(\frac{PR}{\hbar}\right) {}^c\chi^{3+}_{\kappa,\lambda,\mu} - \frac{\kappa+2}{\kappa+1} Z_\kappa\left(\frac{PR}{\hbar}\right) {}^c\chi^{3-}_{\kappa,\lambda,\mu}\right) \\ \frac{\varepsilon_J}{R}\left(\frac{\kappa}{\kappa+1} Z_{\kappa+2}\left(\frac{PR}{\hbar}\right) {}^c\chi^{0+}_{\kappa,\lambda,\mu} - \frac{\kappa+2}{\kappa+1} Z_\kappa\left(\frac{PR}{\hbar}\right) {}^c\chi^{0-}_{\kappa,\lambda,\mu}\right) \end{pmatrix} = {}^2\psi^{P}_{\kappa,\lambda,\mu}(R,\alpha,\beta,\gamma).$$

The Wave Equation in p-space.

Corresponding to (3·1) we postulate the wave equation in p-space,

$$(8.1)\quad \left(\beta_k x^k - iR\beta'\right)\phi^R = 0 ,$$

where

(8.2) $$\beta_l = g_{lm}\beta^m,$$

and β' is similar to β with $\varepsilon_1', \varepsilon_2'$ replacing ε_1 and ε_2, and (8.3) .. $\varepsilon_1'\varepsilon_2' = -1$.

Each component of ϕ^R satisfies

(8.4) $$(p^2 - t^2 - R^2)F = 0 .$$

We introduce polar co-ordinates, as in R-space

(8.5)
$$\begin{aligned} p_1 &= P\cosh\alpha' \sin\beta' \cos\gamma' \\ p_2 &= P\cosh\alpha' \sin\beta' \sin\gamma' \\ p_3 &= P\cosh\alpha' \cos\beta' \\ p_0 &= P\sinh\alpha' . \end{aligned}$$

As in IV the representation of the angular momentum operator in p-space is denoted by an accent.

The wave equation can be expressed in polar co-ordinates, analogous to (3-5)

(8.6) $$\left\{ -\frac{1}{2P^2}\cdot\frac{i}{\hbar}\left[(\beta_k p^k).\, K'^2\right] + \frac{\hbar}{i}\left(\frac{1}{P}\frac{\partial}{\partial P} + \frac{1}{2P^2}\right)(\beta_k p^k) + iR\beta' \right\} \phi^R = 0 .$$

From a consideration of the rule formulated in (III, 2·3), the simultaneous proper function of ${}^sM_2'$, ${}^sM'^2$, ${}^sK'^2$ can be deduced from those of ${}^sM_2$, ${}^sM^2$, ${}^sK^2$

Let such a function be

$$\begin{pmatrix} \omega_1 \\ \omega_2 \\ \omega_3 \\ \omega_0 \end{pmatrix} .$$

Then the two sets of proper functions are

(A) Those having proper values $\hbar\mu$, $\hbar^2\lambda(\lambda+1)$, $\hbar^2(\kappa+1)^2$ for ${}^sM_2'$, ${}^sM'^2$, ${}^sK'^2$ are

$$(8.7)\quad \begin{cases} {}^a\omega^{1\pm}_{\kappa,\lambda,\mu} = \frac{\lambda}{\lambda+1}\Omega^{1-}_{\kappa\pm1,\lambda,\mu} + \frac{(\lambda+1\pm\overline{\kappa+1})(\lambda+2\pm\overline{\kappa+1})}{(2\lambda+1)(\lambda+1)^2}\Omega^{1+}_{\kappa\pm1,\lambda,\mu} \\ {}^a\omega^{2\pm}_{\kappa,\lambda,\mu} = i\,\frac{\lambda\mp1\pm(\kappa+1)}{\lambda(\lambda+1)} \\ {}^a\omega^{3\pm}_{\kappa,\lambda,\mu} = 0 \\ {}^a\omega^{0\pm}_{\kappa,\lambda,\mu} = 0 \end{cases} \begin{cases} {}^b\omega^{1\pm}_{\kappa,\lambda,\mu} = -{}^a\omega^{2\pm}_{\kappa,\lambda,\mu} \\ {}^b\omega^{2\pm}_{\kappa,\lambda,\mu} = {}^a\omega^{1\pm}_{\kappa,\lambda,\mu} \\ {}^b\omega^{3\pm}_{\kappa,\lambda,\mu} = 0 \\ {}^b\omega^{0\pm}_{\kappa,\lambda,\mu} = 0 \end{cases} \begin{cases} {}^c\omega^{10}_{\kappa,\lambda,\mu} = 0 \\ {}^c\omega^{20}_{\kappa,\lambda,\mu} = 0 \\ {}^c\omega^{30}_{\kappa,\lambda,\mu} = \frac{\lambda}{2\lambda+1}\Omega^{1-}_{\kappa,\lambda,\mu} - \frac{(\lambda-\kappa)(\lambda+\kappa+2)}{(2\lambda+1)(\lambda+1)^3}\Omega^{1+}_{\kappa,\lambda,\mu} \\ {}^c\omega^{00}_{\kappa,\lambda,\mu} = -2f'_{\kappa,\lambda,\mu}\,. \end{cases}$$

(B) Those having proper values $\hbar\mu,\ \hbar^2\lambda(\lambda+1),\ \hbar^2\kappa(\kappa+2)$ **for** ${}^sM'_z,\ {}^sM'^2,\ {}^sK'^2$

$$(8.8)\quad \begin{cases} {}^a\omega^{10}_{\kappa,\lambda,\mu} = \frac{i\lambda^2}{(2\lambda+1)}\Omega^{1-}_{\kappa,\lambda,\mu} + \frac{i(\lambda-\kappa)(\lambda+\kappa+2)}{(2\lambda+1)(\lambda+1)^2}\Omega^{1+}_{\kappa,\lambda,\mu} \\ {}^a\omega^{20}_{\kappa,\lambda,\mu} = -\Omega^{10}_{\kappa,\lambda,\mu} \\ {}^a\omega^{30}_{\kappa,\lambda,\mu} = 0 \\ {}^a\omega^{00}_{\kappa,\lambda,\mu} = 0 \end{cases} \begin{cases} {}^b\omega^{10}_{\kappa,\lambda,\mu} = -{}^a\omega^{20}_{\kappa,\lambda,\mu} \\ {}^b\omega^{20}_{\kappa,\lambda,\mu} = {}^a\omega^{10}_{\kappa,\lambda,\mu} \\ {}^b\omega^{30}_{\kappa,\lambda,\mu} = 0 \\ {}^b\omega^{00}_{\kappa,\lambda,\mu} = 0 \end{cases} \begin{cases} {}^c\omega^{1\pm}_{\kappa,\lambda,\mu} = 0 \\ {}^c\omega^{2\pm}_{\kappa,\lambda,\mu} = 0 \\ {}^c\omega^{3\pm}_{\kappa,\lambda,\mu} = \frac{\lambda^2}{2(2\lambda+1)}\Omega^{1-}_{\kappa\pm1,\lambda,\mu} - \frac{(\lambda+1\pm\overline{\kappa+1})(\lambda+2\pm\overline{\kappa+1})}{2(2\lambda+1)(\lambda+1)^2}\Omega^{1+}_{\kappa\pm1,\lambda,\mu} \\ {}^c\omega^{0\pm}_{\kappa,\lambda,\mu} = (\lambda\mp1\pm(\kappa+1))\,f'_{\kappa\pm1,\lambda,\mu}\,. \end{cases}$$

Where the accent denotes that α,β,γ are to be replaced by α',β',γ' in the expressions for f and Ω .

Two independent solutions of the wave equation are obtained

$$(8.9)\quad {}^1\phi^R(\rho,\alpha',\beta',\gamma') = \begin{pmatrix} \frac{1}{\rho}Z_{\kappa+2}\,{}^a\omega^{1+}_{\kappa,\lambda,\mu} - \frac{1}{\rho}Z_\kappa\,{}^a\omega^{1-}_{\kappa,\lambda,\mu} \\ \frac{1}{\rho}Z_{\kappa+2}\,{}^a\omega^{2+}_{\kappa,\lambda,\mu} - \frac{1}{\rho}Z_\kappa\,{}^a\omega^{1-}_{\kappa,\lambda,\mu} \\ \frac{2i\epsilon'_1}{\rho}Z_{\kappa+1}\,{}^c\omega^{30}_{\kappa,\lambda,\mu} \\ \frac{2i\epsilon'_1}{\rho}Z_{\kappa+1}\,{}^c\omega^{00}_{\kappa,\lambda,\mu} \end{pmatrix};\quad {}^2\phi^R_{\kappa,\beta,\gamma} = \begin{pmatrix} \frac{1}{\rho}Z_{\kappa+1}\,{}^a\omega^{10}_{\kappa,\lambda,\mu} \\ \frac{1}{\rho}Z_{\kappa+1}\,{}^a\omega^{20}_{\kappa,\lambda,\mu} \\ \frac{\epsilon'_1}{\rho}\left(\frac{\kappa}{\kappa+1}Z_{\kappa+2}\,{}^c\omega^{3+}_{\kappa,\lambda,\mu} - \frac{\kappa+2}{\kappa+1}Z_\kappa\,{}^c\omega^{3-}_{\kappa,\lambda,\mu}\right) \\ \frac{\epsilon'_1}{\rho}\left(\frac{\kappa}{\kappa+1}Z_{\kappa+2}\,{}^c\omega^{0+}_{\kappa,\lambda,\mu} - \frac{\kappa+2}{\kappa+1}Z_\kappa\,{}^c\omega^{0-}_{\kappa,\lambda,\mu}\right) \end{pmatrix}$$

where the argument of each Bessel Function is $\frac{PR}{\hbar}$.

The reciprocal functions for the meson equation have been determined, as in III and V. However there is difficulty as regards the correct definition and normalization of reciprocal functions, and this point must be clarified before further work can be done.

I have to express my thanks to Dr. K. Fuchs for guidance in writing this paper.

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